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JUL - 5 1996

UNOCAL⑦⑥

July 1, 1996

Thomas I. Hall
Staff Geologist
Corporate Environmental
Remediation & Technology

Mr. Rob Watson
Illinois Environmental Protection Agency
Manager Corrective Action Unit
Permit Section
Bureau of Land
2200 Churchill Road, P.O. Box 19276
Springfield, IL 62794-9276

OVERNIGHT DELIVERY

Re: **1978030004 -- WILL COUNTY**
UNO-VEN REFINERY
ILD041550567
RCRA Permit Log No. 162
RCRA CLOSURE FILE

Dear Mr. Watson:

Enclosed are three copies of the Conceptual Plan for a Vegetative Cover that presents an alternative closure option for the Land Treatment Facility (LTF) at the UNO-VEN Refinery, Lemont, Illinois.

This Conceptual Plan is provided as an information package summarizing regulatory and preliminary technical rationale for the utilizing a vegetative cover closure at the UNO-VEN refinery LTF. The report is meant as a tool to assist the Illinois EPA in evaluating the vegetative cover closure approach as a site-specific solution.

The conceptual plan provides data to support the six reasons why we believe a vegetative cover would be an appropriate closure method at the UNO-VEN site:

- The approach satisfies regulatory requirements applicable to closure of a land treatment facility;

- The treatment zone soils have demonstrated an ability to support vegetation;

- A risk assessment evaluation revealed that there is no unacceptable human or ecological risk from potential direct exposure if the treatment zone is not covered by soil;

- The proposed vegetative cover will be effective in minimizing wind and water erosion;

- The site conditions and scientific literature indicate that the proposed cover will be effective in minimizing potential for groundwater impacts because of reduced infiltration and enhanced degradation, transformation and immobilization of waste constituents; and,

- Post-closure monitoring will evaluate performance on a frequent basis.

The Conceptual Plan has been evaluated by Dr. Larry Erickson, Professor and Director of the Center for Hazardous Substance Research at Kansas State University, and Dr. Jerald Schnoor, Professor and Co-Director of the Center for Global and Regional Environmental Research at The University of Iowa. Copies of letters from Dr. Erickson and Dr. Schnoor, endorsing the use of a vegetative cover at the LTF, are enclosed for your reference.

Unocal would like to extend an offer to sponsor a seminar for the Illinois EPA on the general concepts of phytoremediation and current uses of vegetative covers. We will make arrangements to have Professors Erickson and Schnoor attend the meeting and present their research. As we discussed, the best possible time to schedule the seminar is in late July or early August. I hope that you will accept our offer.

We believe that the vegetative cover proposed in the Conceptual Plan is an effective approach that meets the regulatory requirements applicable to closure of a land treatment facility. It is our desire to gain IEPA approval to move forward with the final design of the vegetative cover.

We are looking forward to presenting this idea to you in full detail. I will call you in a few days to arrange a formal meeting. In the mean time, please call me at (847) 310-6806 if you should have any questions.

Sincerely yours,

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ilfy3a03.doc

cc: J. H. Garretson w/o encl.
       J. J. Dean w/o encl.
       C. Harmon, UNO-VEN w/o encl.
       N. Nedeau, UNO-VEN w/o encl.
       G. Cipriano, Geraghty & Miller, 35 E. Wacker Dr., Suite 1000, Chicago, IL 60601 w/o encl.
       file

Department of Chemical Engineering

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FAX: 913-532-7372

May 16, 1996

Mr. Tom Hall
Staff Geologist
Corporate Environmental Remediation and Technology
UNOCAL
2300 Barrington Road, Suite 500
Hoffman Estates, IL 60195

Dear Mr. Hall:

Based on the meeting on October 31, 1995 at your
facility, the visit to the site and the review of the
site characterization report and the conceptual plan
for a vegetative cover, the land treatment facility,
UNO-VEN Refinery, Lemont, IL looks like a good site to
implement innovative vegetative technologies. The
site should be managed to immobilize the inorganic
contaminants (lead, chromium and arsenic) in place
through evapotranspiration of rainfall by plants and
by management of pH and soil chemistry.

There is significant interest in this approach
because of the potential savings that can be obtained
and because of the effectiveness observed in other
applications of vegetation.

Sincerely yours,

Larry E. Erickson
Professor and Director
Center for Hazardous
Substance Research
Phone: 913-532-4313

THE UNIVERSITY OF IOWA

June 26, 1996

Mr. Tom Hall
Staff Geologist - UNOCAL
2300 Barrington Road, Suite 500
Hoffman Estates, Illinois 60195

Dear Tom:

I have visited the UNO-VEN Refinery and land farm in Lamont, Illinois, and reviewed the site characterization report and the conceptual plan at the request of Geraghty and Miller. It appears that the 13 acre site is a good candidate for phytoremediation for the following reasons:
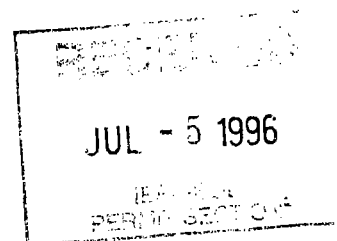
- Vegetation has already invaded and is growing at the site

- Toxicity of the waste materials seems to be relatively low as measured by TCLP procedures

- BTEX compounds in the waste should be amenable to treatment by vegetation

- Mobility of the metals to groundwater is not a significant problem and would decrease due to evapotranspiration

Phytoremediation would allow for continued degradation of organic petrochemicals at the site as opposed to an impermeable cover that would create anaerobic conditions. Please let me know if you have other questions.

Sincerely yours,

Jerald L. Schnoor
Professor and Co-Director

JLS:jsf

CONTENTS

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APPENDICES

GERAGHTY & MILLER, INC.

1.0 **INTRODUCTION**

Geraghty & Miller has prepared this "Conceptual Plan for a Vegetative Cover, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois" (Conceptual Plan) to present the fundamental regulatory and technical basis for the vegetative cover closure approach. The UNO-VEN Company (UNO-VEN) and the Unocal Corporation (Unocal) have submitted a Resource Conservation and Recovery Act (RCRA) Part B permit application (Geraghty & Miller 1995a) to conduct an in-place closure of the Land Treatment Facility (LTF). The vegetative cover closure approach will be fully presented to the Illinois Environmental Protection Agency (IEPA) in a revised closure plan for UNO-VEN's Part B permit application, if IEPA concurs that the vegetative closure approach meets the necessary closure performance requirements.

The closure plan currently included within the Part B permit application describes construction of a 30-inch thick soil cover system as the selected closure option. However, subsequent evaluations indicate that a vegetative cover has a high potential to be a viable alternative to the 30-inch thick soil cover system described in the closure plan. Vegetative covers have been successfully utilized at other sites to provide low-cost, manageable covers which produce stable soils, sustainable ecosystems, wildlife habitats and marketable crops, while preventing groundwater and surface water pollution.

This Conceptual Plan is meant to be an "information package" summarizing regulatory and preliminary technical rationale for the vegetative cover closure approach to assist IEPA in evaluating the vegetative cover closure approach as a site-specific solution. Copies of recent articles by leading experts on vegetative remedies cited in this Conceptual Plan are included in Appendix A.

There are six primary reasons why Geraghty & Miller and Unocal
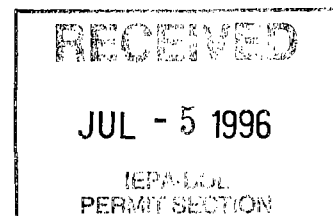
GERAGHTY & MILLER, INC.

believe a vegetative cover would be an appropriate closure method at the UNO-VEN site:

- The approach satisfies regulatory requirements applicable to closure of land treatment units;

- The treatment zone soils have demonstrated ability to support vegetation;

- Based on a preliminary risk assessment, there is no unacceptable human or ecological risk from potential direct exposure if the treatment zone is not covered by soil;

- The proposed vegetative cover will be effective in minimizing wind and water erosion.

- The site conditions and scientific literature indicate that the proposed cover will be effective in minimizing potential for groundwater impacts because of reduced infiltration and enhanced degradation, transformation and immobilization of waste constituents; and,

- Post-closure monitoring will evaluate performance on a frequent basis.

These points will be discussed in detail in subsequent sections.

This Conceptual Plan is organized into seven sections of text, plus references, figures and appendices. A brief description of each section is as follows.

Section 1.0, Introduction presents the purpose and organization of this Conceptual Plan.

Section 2.0, Site Background describes the Site conditions, and presents information on the history of the Site and the results of prior investigations.

Section 3.0, Site-Specific Vegetative Cover provides a general description of the vegetative cover presented for consideration at the UNO-VEN site.

Section 4.0, Regulatory Rationale reviews various regulatory sources to gain insight into the regulatory meaning of the term "vegetative cover" used in Illinois hazardous waste regulations relative to closure requirements for land treatment units.

Section 5.0, Technical Rationale describes the engineering control, advantages and disadvantages provided by a vegetative cover. Scientific literature, case studies and the site-specific risk assessment are also included in this section.

Section 6.0, Summary outlines the information set forth in this Conceptual Plan.

Section 7.0, References lists the literary sources utilized in the compilation of this information package.

2.0 SITE BACKGROUND

The UNO-VEN refinery (ILD0041550567) is located at 135th Street and New Avenue in Lemont, Will County, Illinois, about 25 miles southwest of downtown Chicago and 2 miles southwest of Lemont, Illinois. The LTF is bounded by the UNO-VEN refinery tank farm to the north, farm fields to the east and south, and undeveloped land to the west. Figure 2-1 shows the location of the site on the U.S. Geological Survey topographic map.

The UNO-VEN refinery has a rated capacity of approximately 153,000 barrels per day, and produces a number of products, including gasoline, furnace oils, jet fuel, diesel fuel, specialty naphthas, and petroleum coke (ERM 1988).
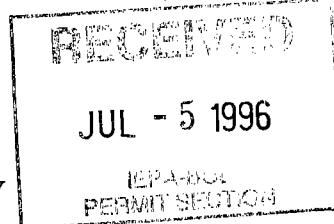
2.1 DESCRIPTION OF LAND TREATMENT FACILITY

Land application of wastes is a treatment method in which soil bacteria are used for the degradation of the oils and greases and the transformation of inorganic constituents, such as sulfide. The soil is managed by proper waste application rates and cultivation to maintain aerobic conditions in the treatment zone. Careful monitoring and management of the land treatment plots provides for degradation, transformation, or immobilization of the waste constituents within the treatment zone.

The UNO-VEN landfarm consists of four discrete plots (referred to as Areas I through IV) used for waste treatment (Figure 2-2). Area I opened in 1973 and Areas II, III, and IV opened in 1980. The LTF is located within an area that occupies approximately 28 acres, of which approximately 13.5 acres was used for waste application. The remaining land includes untilled buffer zones around each landfarm plot, roads, and a non-hazardous waste storage and decant basin. Surface water drainage is generally to the west via an intermittent stream that ultimately leads to the Stormwater Basin (SWB) at the UNO-VEN refinery, located approximately 1 mile west of the LTF.

The wastes which have been applied within the land treatment area include five nonhazardous wastes (clear well sludge, cooling tower sludge, heavy oil sludge, SWB dredgings, and water/wastewater sludge), and one listed hazardous waste (API separator sludge, K051). API separator sludge made up less than one percent of the total wastes land treated and has not been applied since September 1981. The majority of the wastes land treated were SWB dredgings, and water and wastewater treatment sludge. The last application of nonhazardous wastes by Unocal occurred in 1989. An additional 8,570 dry tons of dewatered SWB dredgings were placed on Landfarm Area I in 1995 by UNO-VEN pursuant to an approved closure plan modification (Geraghty & Miller, 1995b; Bakowski, pers. comm. 1995).

The soils at the LTF consist of fine textured soils in the Ashkum (silty clay loam), Blount (silt loam), Chatsworth (silty clay) or Morley (silt loam) soil series, and are suited for agricultural production of corn, soybeans, small grains, grasses, and legumes. The subsoils and underlying glacial sediments below the surface soils to a depth of approximately 60-inches have textures described as silty clay to silty clay loam (USDA 1975).

The treatment zone is distinguished from the undisturbed zone by a change in soil color (Geraghty & Miller 1995c). The treatment zone color is described as dark brown-gray to black. The undisturbed zone is a light brown with varying degrees of rust colored mottling. The treatment zone thickness ranges from not present to 5.0 ft with an average of less than 2.0 ft (Geraghty & Miller 1995c). The lowest portion of this treatment zone is underlain by at least 30 ft of relatively low permeability glacial till and is approximately 60 ft above the seasonal high static water level elevation in the uppermost aquifer. Perched groundwater has been found in discrete intervals which occur at variable depths within the clay till above the static water level elevation of the uppermost aquifer.

2.2 SITE CHARACTERIZATION

A limited site characterization study to evaluate potential LTF impacts to the environment was performed as part of the "Phase I" closure activities conducted in 1988 by ERM (ERM 1989). Additional site characterization tasks were performed by Geraghty & Miller on behalf of Unocal Corporation at the LTF during the period from October 1994 through February 1995 (Geraghty & Miller 1995c). The characterization tasks performed by Geraghty & Miller were conducted to support plans for in-place closure of the LTF.

Data obtained during the site characterization study conducted by Geraghty & Miller indicate that metals concentrations in the treatment zone soils is the primary environmental concern at the LTF. Additional conclusions which can be drawn from the site characterization study conducted by Geraghty & Miller are as follows:

- The treatment zone thickness ranges from 0 ft to 5 ft based on data from 29 soil borings completed by Geraghty & Miller (1995a) and a previous investigation by ERM (1989).

- The treatment zone soils contain some Skinner List VOCs and SVOCs in localized areas.

- The treatment zone soils are not characteristically hazardous.

- Arsenic is the only metal with any evidence of migration from the treatment zone into the undisturbed zone. The impacts were present in only 6 of the 29 soil borings and are limited to the upper 4 ft of the shallow undisturbed zone.

- The undisturbed zone soils are not characteristically hazardous.

- In localized areas, surficial soils around the landfarm area perimeters contain elevated concentrations of a few metals, primarily chromium.

- Soils outside the landfarm area perimeters are not characteristically hazardous.

- The ongoing perched zone groundwater monitoring is adequate for detection of potential landfarm impacts. There has been no evidence to date of a release of hazardous waste or hazardous waste constituents into perched groundwater.

- Stream sediment impacts are limited to SVOCs which occur primarily in the portion of the stream channel directly adjacent to the landfarm areas. The SVOC impacts were negligible at the furthest downstream sampling location of the LTF near the western property boundary .

3.0 PROPOSED VEGETATIVE COVER

The vegetative cover closure approach will promote continuing in-situ treatment within the treatment zone to transform and immobilize metals, and, degrade or immobilize hydrocarbon constituents. In addition, vegetation is an effective cover to minimize water and wind erosion and transport of waste constituents. A vegetative cover is a form of what has become known as phytoremediation. The proposed vegetative cover will also be protective of groundwater by the planting of hybrid poplars and grasses to a density and depth such that the vegetation develops an extensive root system which stores moisture entering the ground. Uptake of water by the hybrid poplars and grasses through their extensive root systems, frees pore space in the soil for precipitation storage, thus managing infiltration and soil moisture. During the transpiration process, the deep, dense root system of the hybrid poplars and grasses collect water for transport to the leaves where the water returns to the atmosphere.

At the UNO-VEN LTF, hybrid poplar trees (Imperial Carolina, Populus deltoides nigra DN-34) will be planted at a density of approximately 2,000 trees per acre. Trees will be planted with one foot of distance between each tree within each row and six feet of distance between rows. The trees will be planted as small cuttings inserted approximately two feet into the landfarm plot soils using a trencher which slices into the ground cover and causes minimal disturbance. Lime and nitrogen/phosphorus/potassium will be included as soil amendments at the time of planting, if necessary. A ground cover of alfalfa or fescue will also be established during planting activities.

The hybrid poplar roots are expected to become established within the first year. The expected growth rate of the hybrid poplars is 4 to 6 feet in each of the first three years; eventually, the trees will grow to 25-35 feet in height and roots will grow down into the landfarm plot soils to depths of approximately 8 feet.

The site will require active management for the first three years. Dead trees will be replaced and the grass cover will be replanted if it fails to become established. Irrigation may be needed for the first two growing seasons to provide adequate moisture for establishment of the tree root systems. After the first three years of growth, minimal maintenance activities will be required. Plant health monitoring, occasional pruning, thinning of the tree population and periodic mowing between rows will be necessary to curtail growth of unwanted tree species. Mowings may be mulched and left in-place. A sustained poplar tree density of at least 1,450 trees per acre will be considered acceptable to achieve the desired cover system performance. Grass which becomes shaded out after the first three years will not be replanted.

The recommended monitoring scheme consists of quarterly sampling of the upgradient and downgradient wells in the perched zone and regional water table aquifer to verify that there is no migration of waste constituents to groundwater. Groundwater samples will be collected and analyzed for parameters outlined in Section 5.3. In the late summer or early fall seasons, tree leaves will also be monitored to verify that no toxic metals were being uptaken and blown offsite following litter fall. Annual coring of the treatment zone and undisturbed zone soils will be performed to evaluate hydrocarbon degradation and chromium/arsenic mobility.

4.0 <u>REGULATORY RATIONALE</u>

Closure and post-closure requirements for permitted land treatment units include establishment of a vegetative cover as specified in Title 35 of the Illinois Administrative Code, Part 724.380 (35 IAC 724.380), "Closure and Post-Closure Care." A vegetative cover is specified so that the aerobic degradation, transformation, and immobilization processes inherent to land treatment are not impeded during closure and post-closure. The closure and post-closure requirements for land treatment units found in the Illinois Environmental Protection Agency (IEPA) document entitled "RCRA Part B Permit Application Decision Guide" (IEPA, December 1990) also specify a vegetative cover which is consistent with the principles stated in the above regulations (I-1d(6) Closure of Land Treatment Facilities, pg. 59). There is no mention of soil, clay or synthetic caps in association with the vegetative cover in either of the two sources cited above.

Vegetation as a final cover is clearly an option for closure as discussed in the United States Environmental Protection Agency (USEPA) guidance document entitled "Guidance Manual on Hazardous Waste Land Treatment Closure/Post-Closure, 40CFR Part 265" (USEPA 1987). The USEPA (1987) guidance document describes three basic closure approaches for hazardous waste land treatment units: 1) removal of contaminated soil, 2) placement of a final cover, such as a vegetative cover or clay or synthetic cap, and 3) continued groundwater monitoring. Site conditions at the UNO-VEN Refinery in Lemont, Illinois appear to meet the USEPA (1987) criteria for selection of a final cover as the closure method which are as follows:

1. "unsatisfactory migration of constituents from the unit has not occurred;"

2. "environmental site and soil conditions (e.g., moderate to low precipitation and high evapotranspiration, soils with moderate to high sorptive capacity) indicate a moderate to low potential for migration from the unit; and ,"

3. "residual waste concentrations are at low to medium concentrations, exhibit moderate potential for transport in percolating water or in air, and /or are of low residual toxicity"

Additionally, site conditions at the UNO-VEN Refinery in Lemont, Illinois also appear to satisfy the following two additional USEPA (1987) criteria for selection of a vegetative cover as the closure method:

1. "a lower potential for migration to groundwater exists such that the primary purpose of the cover would be to minimize direct contact and inhalation of residual constituents and to control erosion and run-off; and "

2. "there may be potential for continued in-place treatment of waste residuals in the soil system during the post-closure period."

5.0 TECHNICAL RATIONALE

As previously stated, a vegetative cover has a high potential to be a viable alternative to the cover system currently specified in the closure plan. The preliminary technical basis for this assertion is presented in this section of the document. The information presented also addresses the following initial paraphrased concerns previously expressed by Mr. Jerry Kuhn and Mr. Robert Watson of IEPA's Bureau of Land, Permit Section, RCRA Unit regarding the potential disadvantages of the phytoremediation approach:

- Will the uncovered treatment zone support vegetation?

- Would a vegetative cover be effective in minimizing infiltration of rainfall, thus minimizing leaching of metals, and would there be preferential infiltration along openings caused by tree roots?

- Are there unacceptable potential human health risks from direct exposure (inhalation, ingestion, dermal contact) to the treatment zone, if it is not covered with soil?

- Will ecological impairment result from exposure of organisms to the treatment zone if it is not covered with soil, or will bioaccumulation occur in organisms ingesting plants with elevated metals concentrations due to uptake of metals from the uncovered treatment zone?

Specific topics in this section include a discussion of the anticipated effectiveness of a vegetative cover to protect the environment supported by references to scientific literature and site-specific experience. Results of a preliminary risk assessment are also presented in this section to evaluate human health and ecological risks for the vegetative cover closure scenario. Proposed monitoring to evaluate the vegetative cover performance on a frequent basis is also outlined.

5.1 EFFECTIVENESS OF A VEGETATIVE COVER

The vegetative cover is anticipated to be effective in protecting the environment because of the following characteristics which are discussed further below:

- Treatment zone soils will support vegetation over the long-term with limited maintenance

- Trees and grasses create a canopy above ground and also physically interlock with soils to minimize wind and water erosion

- Uptake and loss of soil moisture by vegetation (particularly trees) during transpiration and the creation of a canopy is protective of groundwater by reducing infiltration

- Plants either directly or indirectly degrade, transform or immobilize many petroleum hydrocarbon compounds and metals to further protect groundwater and reduce residual toxicity of the treatment zone

5.1.1 Ability to Support Vegetation

The effectiveness of a vegetative cover will be largely a function of how well the treatment zone can support vegetation. The treatment zone soils at the UNO-VEN LTF presently support the growth of volunteer and pioneer vegetation species. The current vegetation is present even though there has been no effort to establish or maintain vegetation since placement of the last waste on the landfarm plots in 1989. Thus, site specific experience indicates that the treatment zone is capable of supporting vegetation over the long term with minimal maintenance.

In extreme conditions, soil amendments that reduce the bioavailability of metals and metals-tolerant plant species have been used at other sites to successfully establish a vegetative cover (Pierzynski et al. 1994). The studies conducted at the Galena Superfund

site in the tri-state mining region (Kansas, Missouri, Oklahoma) demonstrate the soil chemical changes induced by soil amendments designed to reduce metal bioavailability (Pierzynski et al. 1994). The site consists of a large area which is nearly void of vegetation and contains numerous piles of chat (rock waste material generated from the initial processing of ore). Remedial action for the site required the establishment of vegetation to control erosion and runoff. Various organic waste amendments were added to the soil cover to evaluate the vegetative responses in a chat material seeded with native grasses and leguminous forbs. The various amendments aided in enhancing plant growth in contaminated soil and the naturally occurring mycorrhizal fungi proved effective in reducing metal bioavailability (Pierzynski et al. 1994). Hybrid poplar trees have also been successfully established in mine tailings at the Whitewood Creek Superfund site (Pierzynski et al. 1994).

5.1.2 Minimization of Wind and Water Erosion

Standard engineering design for various site restoration scenarios from road construction projects to hazardous waste landfill caps has long recognized the importance of establishing and maintaining vegetation to minimize wind and water erosion. Applications now include the use of trees as part of the vegetative cover for landfills and in some soil or waste environments with high metals concentrations (Licht and Madison 1995; Pierzynski et al. 1994). At the Lakeside Reclamation Landfill near Beaverton, Oregon, approximately 20 tree varieties were planted as part of a low cost, manageable cover (Licht and Madison 1995). Vegetative covers with trees have also been installed at several Iowa Subtitle D landfills as either the final cover or on a previously constructed cap to effectively stabilize the soils (Licht and Madison 1995). The Whitewood Creek Superfund site, an eighteen-mile stretch of surface water and groundwater in the Black Hills of South Dakota, is contaminated with arsenic and cadmium resulting from 130 years of gold mining activity. In April 1991, an experimental plot of 3,100 hybrid poplar

trees was planted to evaluate several potential environmental benefits including stabilization of soils and prevention of wind-blown dust (Pierzynski et al. 1994).

5.1.3 Groundwater Protection

The proposed vegetative cover is anticipated to be effective in protecting groundwater by reducing the amount of infiltration and by promoting the degradation, transformation or immobilization of waste constituents in the treatment zone.

The hybrid poplars and grasses uptake water through their extensive root systems and freeing pore space for precipitation storage. During the transpiration process, the deep, dense root system of the hybrid poplars and grasses also returns water back to the atmosphere. Transpiration will typically exceed rainfall during the growing season such that the plants remove water stored in the root zone soils. This dehydrating action provides water storage capacity during winter dormancy. Thus, the vegetative cover reduces infiltration to groundwater (Licht and Madison 1995). Vegetative covers consisting of trees and grasses have been utilized at numerous landfill sites to prevent creation of leachate (Licht and Madison 1995).

A site specific hydrologic analysis utilizing the HELP model was conducted to determine the infiltration quantities of a vegetative cover with Poplar trees. The model results were then compared to the cover system currently described in the closure plan (30-inch thick soil cover). The infiltration estimates for both scenarios are presented in Appendix C. The HELP model input included the same native soil characteristics that were utilized in the model for the final soil cover system. Although the native soils contain silt and clay which have a low hydraulic conductivity, in both cover alternatives, a more conservative approach was adopted since a majority of the landfarmed material has been stormwater basin sediments which possibly consist of a coarser grain material with a greater hydraulic conductivity. The amount of infiltration calculated by this model

may be greater than the actual because of the assumed greater permeability of landfarm plot soils compared to the native clayey soils. The specific HELP model input parameters for the vegetative cover which varied from that of the soil cover system include the following:

- The native soil layer thickness in the poplar tree model was increased to ten feet and was divided into two layers, 30-inch and 90-inch to take into account the deeper root zone. (In the soil cover model, the native soil underlying the 30-inch soil cover was input as a 60-inch layer.)

- The maximum leaf area and evaporative zone depth were increased from 2.0 and 20 inches to 3.0 and 96 inches, respectively. The 8-foot deep evaporative zone depth includes root depth and underlying capillary suction (Licht, pers. comm. 1996).

- The grass stand on the surface of the landfarm area was characterized as excellent in the poplar tree model and fair in the soil cover model.

Synthetically generated data for precipitation, temperature, and solar radiation using coefficients for Chicago, Illinois were utilized in both model runs. The average annual total percolation/leakage through the native soil materials (Layer 2) calculated by the HELP model is essentially the same for both the soil cover and vegetative cover at 3.4 inches, or approximately 10 percent of the average annual 32.89 inches of precipitation.

Plants reduce the mobility of metals in soils by increasing the organic matter content of soils and by promoting the growth of a consortia of microbes in the rhizosphere (root-soil interface). The results are lower concentrations of mobile metals from adsorption to organic matter and the binding by microbes (Davis et al. 1996; Pierzynski et al. 1994). Plants are also able to biodegrade many petroleum hydrocarbon compounds either through direct metabolic pathways or indirectly by releasing enzymes that breakdown organic compounds (Davis et al. 1996; Schnoor et al. 1995). Plants also promote degradation of many petroleum hydrocarbon compounds by enhancing microbial

activity in the soil through release of exudates to the soil and by pumping oxygen to the root zone (Davis et al. 1996; Schnoor et al. 1995). Metabolism of organic pollutants by mycorrhizae fungi growing in symbiotic association with plants in the root zone can also help to degrade organic compounds in association with bacterial transformations (Davis et al. 1996; Schnoor et al. 1995). In addition, several polynuclear aromatic hydrocarbons may be attenuated in soils by becoming irreversibly bound to fulvic acid/humic acid fractions of the soil (Davis et al. 1996).

5.2 HUMAN HEALTH AND ECOLOGICAL RISKS

Metals were identified as the primary constituents of concern in the treatment zone soils, based on the site characterization study conducted by Geraghty & Miller (Geraghty & Miller 1995b). Therefore, to support this Conceptual Plan, a site-specific risk assessment (Appendix B) was conducted at the UNO-VEN LTF to evaluate whether metals constituents in soils pose a threat to human health or the environment. The Illinois Environmental Protection Agency (IEPA) Tiered Approach to Cleanup Objectives Guidance Document (TACO) (January 1996) was used to identify whether conditions at the UNO-VEN LTF pose a threat to human health under the proposed vegetative cover closure scenario. In addition, an ecological risk assessment (ERA) was completed to evaluate existing metals data for treatment zone soils and plant tissue collected at the site to determine potential site-related ecological effects. The ERA was prepared in accordance with the standard paradigm for predictive ERA as presented in the "USEPA Framework for Ecological Risk Assessment" (USEPA 1992) and the "Ecological Risk Assessment Guidance for Superfund" (USEPA 1994) as adapted to this site.

Human health exposures were evaluated for a site maintenance worker and a construction worker. The maintenance worker is assumed to be working at the LTF 12 days per year for 25 years. The construction worker scenario is to evaluate risks to an individual such as might be involved with the initial installation of the vegetative cover. Exposure for the construction worker assumes the individual is at the LTF 5 days a week

for 9 weeks. In both scenarios, the workers were assumed to incidentally ingest soil and inhale particulates. Both scenarios conservatively assume that the treatment zone soils are bare and do not have a vegetation layer. The risk assessment concluded that no threat to human health is indicated under the assumed exposure conditions from constituent levels detected in the soils at the site. The complete UNO-VEN LTF Risk Assessment is presented in Appendix B.

The ERA (Appendix B) indicates that constituent concentrations detected in, or modeled for, plant tissue at the site are significantly less than plant tissue phytotoxicity benchmarks. The ERA also evaluated potential risk to herbivorous wildlife populations using the Eastern cottontail rabbit as an indicator species. The hazard quotients for the individual metals were all less than 1 and the sum of the hazard quotients (hazard index) was equal to 1. Therefore, constituent concentrations in soil and vegetation the UNO-VEN LTF are unlikely to present a risk to herbivorous receptors.

5.3 PERFORMANCE EVALUATIONS

Groundwater monitoring will be conducted as described in the groundwater monitoring plan submitted with the Part B permit application (Geraghty & Miller 1995a). Sampling of upgradient and downgradient wells (Figure 5-1) will be conducted on a quarterly basis to verify that there is no migration of waste constituents to groundwater. The groundwater monitoring system will consist of six deep wells (UA-1 through UA-6) and six shallow monitoring wells (SW-1 through SW-6). Deep monitoring wells will be sampled and analyzed for total organic carbon (TOC), total organic halogen (TOX), pH and specific conductance; shallow monitoring wells will be sampled and analyzed for chemical oxygen demand (COD), TOC, dissolved arsenic, dissolved lead, dissolved chromium, pH, specific conductance, and temperature.

Annual sampling of tree leaves, the treatment zone and undisturbed zone soils will also be performed. In the late summer or early fall seasons, tree leaves will be collected and analyzed to verify that objectionable quantities of toxic metals are not being uptaken and blown offsite following litter fall. Semiannual collection and analysis of soil core samples from the landfarm will also be conducted to evaluate petroleum hydrocarbon degradation and chromium/arsenic mobility. In this manner, the effectiveness of the vegetative cover will be monitored. If it is determined that the vegetative cover remedial approach is inadequate to achieve site-specific regulatory objectives, corrective action steps will be evaluated immediately.

6.0 SUMMARY

Unocal is proposing to modify the current closure plan for the LTF from a 30-inch thick soil cover system to a vegetative cover. The vegetative cover will consist of hybrid poplar trees and grasses. A vegetative cover will be more consistent with the regulatory requirements for closure of a hazardous waste land treatment unit because it promotes the aerobic degradation, transformation and immobilization processes inherent in land treatment. In contrast, the 30-inch thick soil cover system described in the current closure plan will probably impede the land treatment processes and is not believed to have any substantial advantage over the vegetative cover in terms of meeting the closure performance standards.

The preliminary technical review presented in this plan also indicate that a vegetative cover should be a viable closure method based on the following:

- The treatment zone soils have a demonstrated ability to support vegetation.

- Trees and grasses in combination are being successfully used for cover to minimize wind and water erosion at other sites such as landfills and Superfund sites involving metals contamination.

- Trees and grasses will reduce rainfall infiltration and minimize downward migration of waste constituents, thus protecting groundwater.

- The vegetative cover will reduce the mobility of metals in the treatment zone by adding organic carbon to the root zone and will promote degradation and transformation of petroleum hydrocarbons in the treatment zone.

- The metals concentrations in the treatment zone do not pose any unacceptable human health or ecological risks even if left uncovered, based on the preliminary risk assessment performed.

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SITE LOCATION MAP

UNO-VEN REFINERY
LEMONT, ILLINOIS

FIGURE

2-1
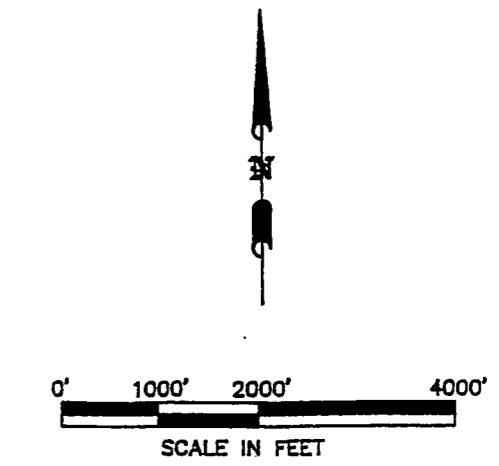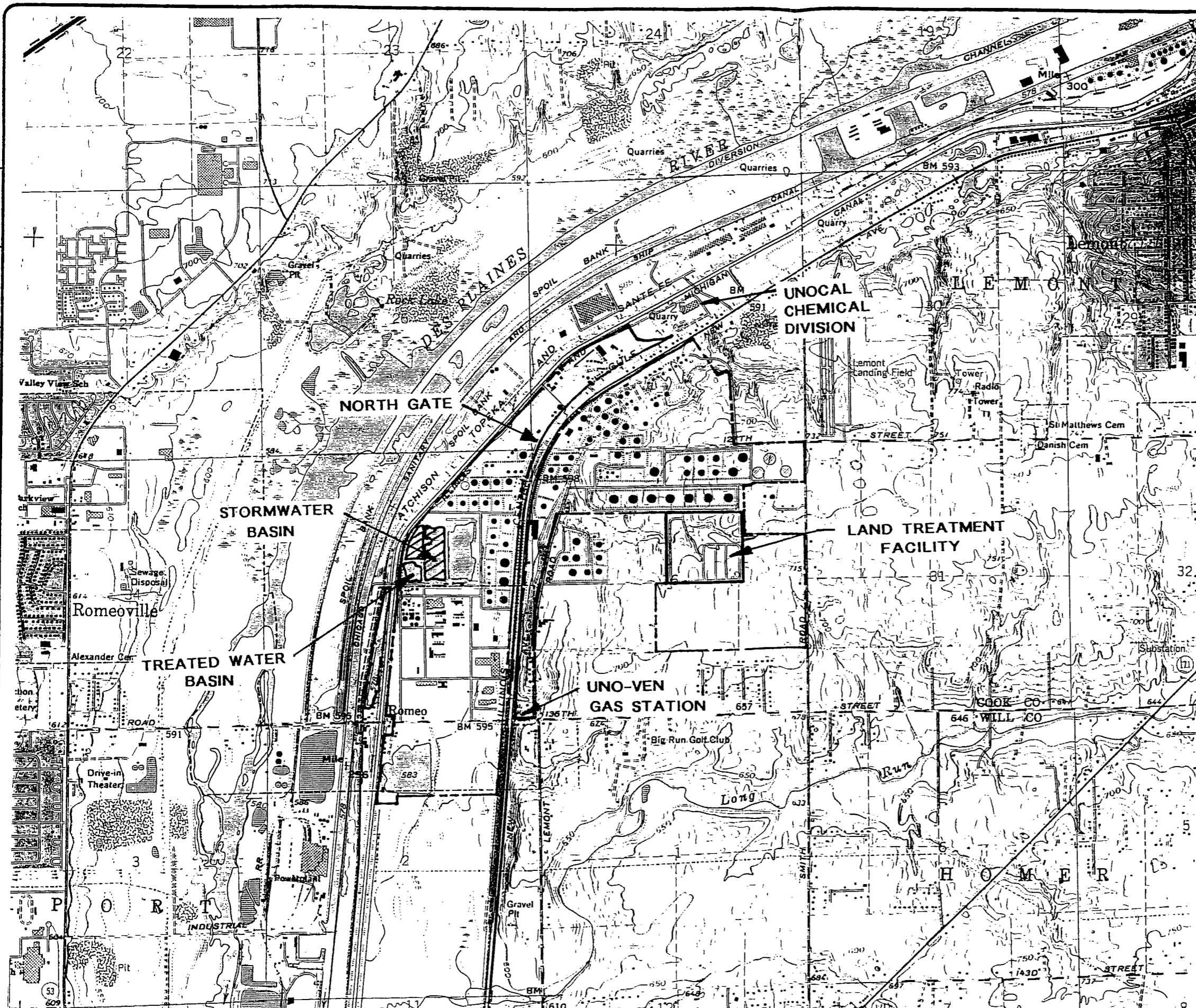
SOURCE:
USGS 7.5 MIN. TOPOGRAPHIC MAP,
ROMEOVILLE, ILLINOIS QUADRANGLE,
1962, PHOTOREVISED 1973 AND 1980.

SCALE IN FEET

0' 1000' 2000' 4000'

—————— REFINERY
PROPERTY
BOUNDARY

N

QUADRANGLE LOCATION

ILLINOIS

GERAGHTY & MILLER, INC.
Environmental Services

Labels on map:
- UNOCAL CHEMICAL DIVISION
- NORTH GATE
- STORMWATER BASIN
- TREATED WATER BASIN
- UNO-VEN GAS STATION
- LAND TREATMENT FACILITY
- Romeoville
- Lemont
- DES PLAINES RIVER
- HOMER
- PORT

T37N
T36N

R10E   R11E

DWG DATE: 4/24/95 | PROJCT NO.: C10345 | DRAWING: C139501-2-1 | FILE NO.: NON-CAD | CHECKED: L. CRAVEN | APPROVED: G. CIPRIANO | DRAFTER: S GOZNER

LEGEND

⬡ LIMITS OF LANDFARM PLOT

— · · · — INTERMITTENT STREAM
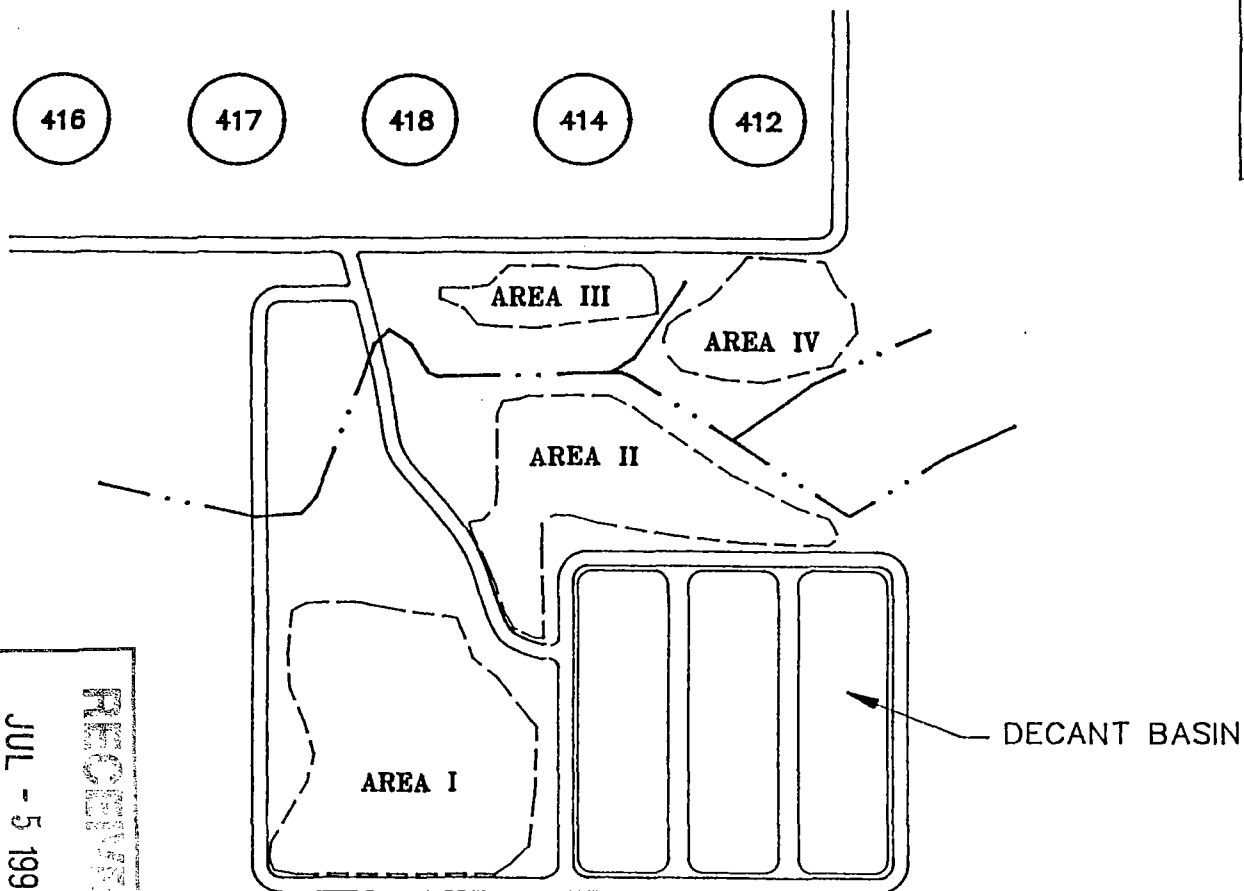
416 417 418 414 412

AREA III

AREA IV

AREA II

AREA I

DECANT BASIN

N

0   400

SCALE IN FEET

SOURCE: ENSR FIGURE 2-1,
FEBRUARY 8, 1989.

GERAGHTY & MILLER, INC.
Environmental Services

LAND TREATMENT FACILITY SITE MAP

UNO—VEN REFINERY
LEMONT, ILLINOIS

FIGURE

2-2
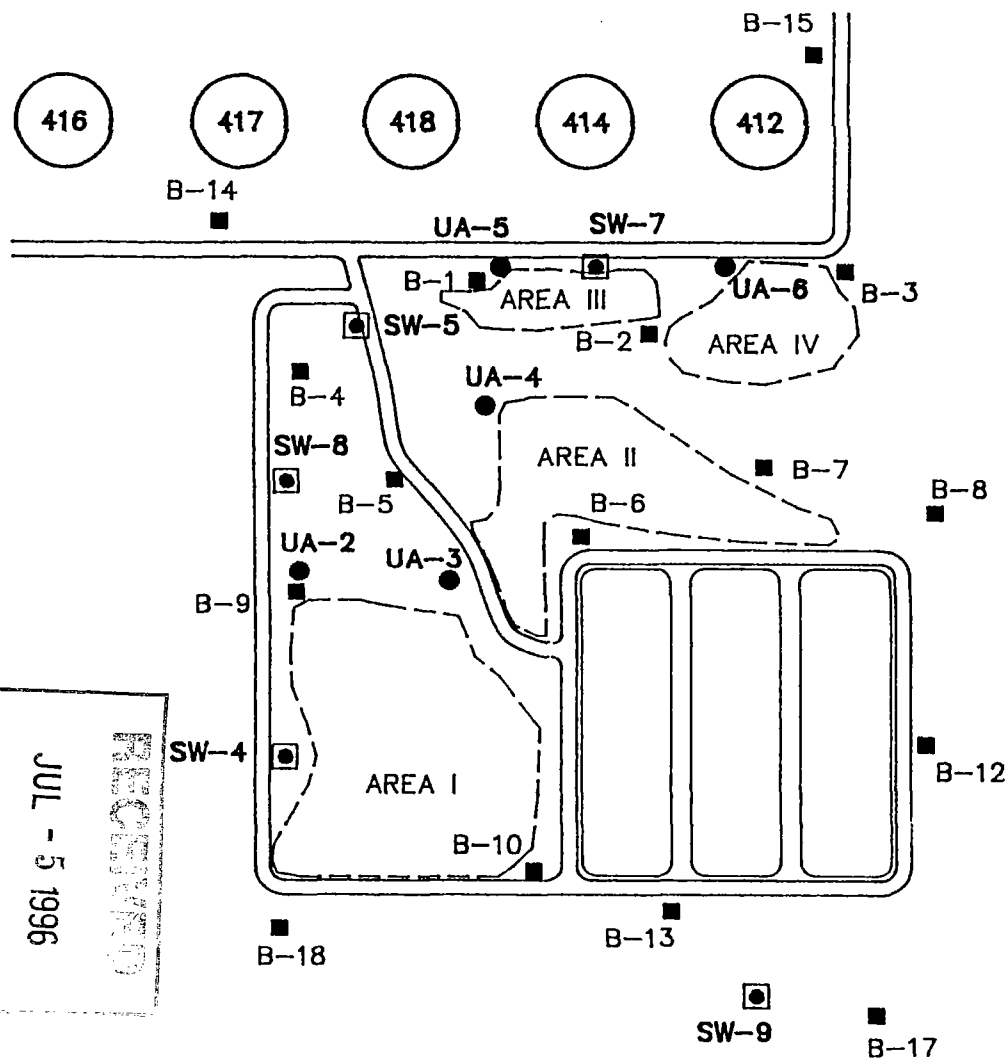
LEGEND

● DEEP MONITORING WELL/ NUMBER

⊡ SHALLOW MONITORING WELL/NUMBER

■ PIEZOMETER/NUMBER

⌐‾¬ LIMITS OF LANDFARM PLOT

416   417   418   414   412

B-15
B-14
UA-5   SW-7
B-1   AREA III   UA-6   B-3
SW-5   B-2   AREA IV
B-4   UA-4   AREA II   B-7   B-8
SW-8   AREA II   B-11
B-5   B-6
UA-2   UA-3
B-9
SW-4   AREA I   UA-1
B-12   SW-1
B-10   B-16
B-18   B-13
SW-9   B-17

JUL - 5 1996

0   400
SCALE IN FEET
SOURCE: ENSR FIGURE 2-1,
FEBRUARY 8, 1989.

GERAGHTY & MILLER, INC.
Environmental Services

MONITORING WELL LOCATION MAP

UNO--VEN REFINERY
LEMONT, ILLINOIS

FIGURE
5-1

APPENDIX A

Scientific Literature

PLANT-BASED BIOREMEDIATION

L.C. Davis, M.K. Banks, A.P. Schwab, Muralidharan Narayanan,
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J.C. Tracy
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Brookings, SD 57007

ABSTRACT

Plant-based bioremediation involves transformation and mineralization of organic contaminants in microbial and plant systems. Microbial biodegradation in the rhizosphere is enhanced by root exudates which supply nutrients. Organic contaminants also may enter plants and be transformed within the plants, in a process called phytoremediation. Evapotranspiration by plants transports water and contaminants to the rhizosphere and helps contain the contaminants within the site boundary.

The basic principles associated with water movement by vegetation are presented. Mathematical models which describe contaminant transport and biodegradation in vegetated soil are described. The bioenergetics of plant-based bioremediation are reviewed with emphasis on impact of vegetation on the magnitude of the microbial population in the rhizosphere. Other soil nutritional considerations which impact plant and microbial growth processes are included. Results are presented for plant-based bioremediation of toluene, phenol, trichloroethylene, and pyrene. Methods to measure intermedia transfer to the gas phase and results for toluene and trichloroethylene are presented. The economics of plant-based remediation which are reported indicate that it is a very inexpensive bioremediation process.

L.C. Davis is in the Department of Biochemistry
M.K. Banks is in the Department of Civil Engineering
A.P. Schwab is in the Department of Agronomy
Muralidharan Narayanan and L.E. Erickson are in the Department of Chemical Engineering

1. Introduction

Although bioremediation as an approach to cleanup contaminated soil and ground water has grown dramatically in the past decade, plant-based remediation, sometimes called phytoremediation (Cunningham and Berti, 1993) is still in its infancy. Anderson et al (1993) and Shimp et al (1993) have provided extensive reviews of the literature through 1991. We will provide some more recent examples from the literature and our own experience and will discuss our present understanding of several roles that plants can play in bioremediation efforts.

As indicated in Table 1, plants may be used to enhance remediation in several ways. The first, on which we will focus most discussion, is to support diverse rhizosphere microbial populations, which are able to metabolize contaminants of concern. This is called indirect phytoremediation by Stomp et al (1994). The second enhancement, which may be considered direct phytoremediation (Stomp et al, 1994) and about which relatively little is known, is to make use of plant metabolic pathways to degrade contaminants (Schnoor et al, 1995, Trapp and McFarlane, 1995). A third direct mode is to use plants to selectively immobilize materials, such as heavy metals (Pierzynski et al, 1994). Finally, through use of genetic engineering techniques, plants may be modified to permit them to degrade contaminants. This is a logical extension of efforts to render plants resistant to herbicides and pesticides.

A recent American Chemical Society Symposium book focuses on the rhizosphere and its role in bioremediation (Anderson and Coats, 1994). A limited number of papers from that symposium are referred to below.

1
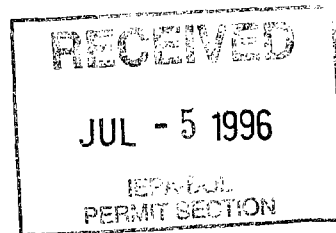
2. Examples of plants in bioremediation

2.1. Chlorinated hydrocarbons.

The pioneering work of Walton and Anderson (1990) studying degradation of trichloroethylene (TCE) has been described in more detail (Anderson and Walton, 1992) and reviewed by Anderson et al (1993). Anderson et al (1993) observed that microbes from rhizosphere soil of several species of plants were able to degrade TCE better than those from non-rhizosphere soil. Even soybeans, which had not been grown in TCE-contaminated soil were able to stimulate its mineralization, when grown in microcosms (flasks). This suggests that the benefits are a function of the plant rhizosphere, not bacterial adaptation to the contaminant.

We will describe our own work with plant based bioremediation of aromatic and chlorinated hydrocarbons (Davis et al, 1993, Erickson et al, 1994b, Muralidharan et al, 1995a,b) below. So far it is the only mesocosm system to be described. Field scale plant-based studies on any contaminant are also very limited in number (Nair et al, 1993, Gatliff, 1994, Schnoor et al, 1995).

2.2. Aromatic hydrocarbons.

Sims and others (Aprill and Sims, 1990, Ferro et al, 1994) explored the ability of grasses to enhance degradation of aromatics. Prairie grasses grown in 25 cm diam x 77 cm long PVC containers stimulated degradation of polycyclic aromatic hydrocarbons (PAHs) (Aprill and Sims, 1990). Crested wheatgrass, when grown in bell jars with recirculation of the air, stimulated degradation of pentachlorophenol (Ferro et al, 1994). Mineralization was enhanced several-fold over that of an unplanted soil. More than 1/3 of the compound ended up in the plants, which suffered some phytotoxicity as a consequence (Ferro et al, 1994).

Specific compounds of the PAH class have been studied in pots in a greenhouse setting by Reilley (1993) and Schwab and Banks (1994). Both anthracene and pyrene disappeared more rapidly in planted than in unplanted soil which had previously been land farmed for disposal of refinery wastes. Alfalfa appeared to be the most effective species with three grasses giving lesser enhancements. In a laboratory study, mineralization of pyrene was enhanced in rhizosphere soil even without plants and was further enhanced by addition of organic acids. Enriched rhizosphere soil gave a five-fold greater release of $^{14}CO_2$ than autoclaved soil. Field studies of several contaminated soils are in progress (M.K. Banks, unpubl. obs.).

Watkins et al (1994) examined ^{14}C-naphthalene mineralization in vegetated and unvegetated microcosms, consisting of 250 mL flasks with 100 g soil. Planted microcosms (with the plant fully contained therein) appeared to increase volatilization and decrease mineralization of the compound. However, the plants were extremely limited for CO_2 during the mineralization phase, with an air supply of 25 mL/min which would allow production of only about 10 mg CH_2O per day. Thus, little root exudate could be supplied by the plants. Volatilization losses precluded using a more natural open system but it is difficult to interpret these results in terms of field situations.

Walton et al (1994) described studies using microcosms (250 mL flasks) planted with white sweet clover (plant tops exposed) and treated with ^{14}C labeled pyrene, fluoranthene, phenanthrene or naphthalene. For all but pyrene, the vegetated microcosms showed a significantly larger fraction of the labeled compound bound to fulvic/humic acid fractions of the soil (up to 40% of extractable labeled material for naphthalene). The important point to note from these studies according to Watkins et al (1994) is that mineralization ought not to be the

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only endpoint considered during remediation studies, because irreversible binding may also be an important mechanism of attenuation.

2.3. Herbicides.

Nair et al (1993) examined mineralization and uptake of atrazine by poplars. Their work was done with rooted cuttings, growing with their root system "sealed" in 1 L flasks in a plant growth chamber. Soil was obtained from Amana, IA, where atrazine had not been previously applied, although in Iowa, atrazine is commonly used on maize crops for weed control. Mineralization within the rhizosphere was monitored by collecting headspace gas from the closed flask at intervals. About 15% of the ring label ^{14}C was released as CO_2, and about 11% remained in the plant after 126 days. The authors cite the unpublished work of Schwarz showing that the plants evolved none of the label as CO_2; that is, the plants themselves do not mineralize the compound. The nature of the accumulated label in the plants is not known. When comparable experiments were done with silica sand as the support medium, instead of a silt loam, a larger fraction of atrazine was taken up by the plants (91% in 22 days). They were transpiring at a much higher rate in the sand medium which could account for the more rapid accumulation. Also, the sand adsorbed less of the atrazine, making more available to the plant.

Shann and Boyle (1994) examined degradation of 2,4-D and 2,4,5-T as influenced by presence of root exudates from monocots vs dicots. A nutrient solution was passed through the root zone of a plant and into a soil column containing the target compound. The exudate of grass nearly doubled the mineralization rate of 2,4,5-T and gave a 50% increase in 2,4-D mineralization while tobacco leachate had little effect. Studies with soil taken from the root zones of monocots vs dicots showed similar significant differences in mineralization rates of the

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same compounds. This indicates that there are likely to be important species differences in the ability of plants to enhance bioremediation by root exudation.

2.4. Other compounds.

Knaebel and Vestal (1992, 1994) examined degradation of several surfactants likely to be found in sewage sludges. A double-chambered microcosm allowed simultaneous exposure of the plant top to ambient conditions and capture on alkali traps of CO_2 from the soil. Both a cationic and an anionic surfactant were mineralized faster, but usually to a lesser extent, in the rhizosphere of corn or soybeans than in an unplanted soil. Soil type had a large effect on rate and extent of mineralization. Pre-binding the surfactant to humic or fulvic acid fractions of soils from different sites greatly altered their relative mineralization rates and extents. Also, a larger fraction of the label was incorporated into biomass in rhizosphere soils. Decreased "turnover" after the initial respiratory burst was apparently the case.

Gatliff (1994) reported successful commercial application of trees to remediation of an aquifer contaminated with ammonium and nitrate. He observed that deeper planting of the trees, i.e. closer to the water table, resulted in better growth and greater N accumulation to leaves. The apparent area of contamination was markedly reduced after two years of tree growth. Costs were significantly lower than for a conventional pump and treat approach in such a tight aquifer. Earlier work by Licht (1990) had demonstrated the feasibility of this approach.

Munitions wastes such as 2,4,6-trinitrotoluene are of considerable interest as candidates for plant-based bioremediation (Schnoor et al, 1995). Wolfe et al (1994) have identified an excreted nitroreductase activity in the root zone of a number of aquatic plants. Transfer of the gene for this enzyme to other species might allow engineering of efficient cleanup.

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Alternatively, Mueller et al (1993) have found that some plant species, at least in tissue culture, are able to sequester considerable quantities of the compound. So far they have shown only partial conversion of the compound, not complete degradation. Bioenergetic considerations, discussed below, make this approach likely to be of limited success, unless it is accompanied by ultimate metabolism of the compounds within the plant to materials that can be incorporated into normal plant structures, or processed for energy yield.

2.5. Heavy metals.

Cunningham and Berti (1993) described efforts to screen plant species for their ability to accumulate lead. Both hemp dogbane (*Apocynum* sp.) and common ragweed (*Ambrosia* sp.) have been observed to grow on highly contaminated sites and to accumulate the metal above the concentration found in the soil. The suggested strategy would be to use plants to collect the metal and then to harvest and appropriately dispose of the plant material. This is further discussed in the paper of Stomp et al (1994).

A recent review considered the potential role of vegetation in remediation of mine waste superfund sites (Pierzynski et al, 1994). Pierzynski and co-workers are attempting to use hybrid poplars to stabilize zinc smelter wastes in Kansas and to immobilize the co-contaminant lead at such sites. Schnoor and others have used a similar approach to control wind-blown dust and soil erosion from mine tailings at Whitewood Creek in South Dakota. Adequate growth is obtained and Cd and As, elements of concern at Whitewood Creek, are not bioaccumulated to high levels in aboveground parts of the trees.

3. The several roles of plants

The main contributions of the plant are likely to be in enhancing rhizosphere remediation, although there are instances of direct contaminant metabolism within the plant (Nair et al, 1993, Trapp and McFarlane, 1995). The following sections consider several plant contributions to rhizosphere function.

3.1. Plants as suppliers of nutrients

Almost all of the hydrogenated carbon on the planet derives from photosynthesis, which is primarily the product of plants and cyanobacteria. In terrestrial systems, plants are the main contributors. Natural organic matter, humic substances, or other organic soil constituents ultimately are derived from plants. Hence, a large fraction of the microbial biomass is dependent on plants for its sources of energy. Microbes have evolved pathways to degrade and extract energy from a vast array of plant-derived products including transformed materials such as crude oil.

In plant-based bioremediation, we are primarily interested in the ability of plants to supply, fairly directly, some of the nutritional and energetic needs of microbes that have abilities to degrade substances that have been classified as pollutants in the environment. Still, we cannot ignore contributions that plants make more indirectly by dead roots, shed leaves which supply a habitat for diverse microbes, and repeatedly recycled plant-derived materials including humic and fulvic acid fractions.

As discussed in Shimp et al (1993), it is difficult to reliably estimate the amount of combined C that plants may contribute annually to the soil via different pathways. A reasonable estimate may be about 1 mole equivalent of glucose exuded and sloughed off from roots per

square meter per year. During respiration, this would yield 6 moles per year of CO_2, half a mole per month, or about 17 mmoles per day. As shown in Table 2, this estimate is in reasonable agreement with the estimates from Erickson et al (1994a, 1995). The photosynthetic rates cited are for an optimally efficient crop with a large root storage component. Actual values may differ widely depending on species and climate. Field measurements do not usually separate carbon released into the soil (e.g. exudates) and carbon deposited on the soil (e.g. leaf fall). The estimate cited, of 1 mole equivalent glucose per year for prairie soils, is in broad agreement with soil respiration estimates (Glinski and Stepniewski, 1985). Ranges of respiration rates of various soils and crops commonly were from 10-100 mmol CO_2 per day per m^2. In an artificially lighted enclosed system containing a sandy soil, we measured rates of 30- 50 mmol CO_2 per day per m^2 immediately after cutting alfalfa plants near the ground (unpubl. obs.). The exudation of 1 mol glucose equivalent per m^2 per year is sufficient to provide maintenance energy requirements for a relatively large microbial population, on the order of 10^8 - 10^9 per gram soil (Erickson et al, 1994a,b, 1995). Active microbes are likely to be concentrated in the vicinity of the roots which are the source of input carbon.

Respiratory activity declines rapidly with depth into the soil, as does the density of rooting by most plants. For typical crops, half of the roots are in the top 1/3 meter of soil (Teare et al, 1973). Federle et al (1986) measured active microbial biomass in several soils and observed in some soils a 100-fold decline in activity within the top half meter. For other soils the decline was less rapid near the top and more rapid below half a meter. It might be most effective to bring contaminants to the active zone where there is potentially a large microbial population able to degrade them. This is discussed below under 'plants as pumps.'

Soil microbes are usually carbon limited. However, when supplied with an abundance of glucose, which is readily metabolized by many microbes, other nutrient limitations become evident (Stotzky and Norman, 1961a,b). Use of a nitrogen fixing legume may allow the plant based system to overcome nitrogen limitation. Mycorrhizae can improve the phosphorus status of host plants which in turn may benefit the rhizosphere population (Shimp et al, 1993). In the soil supplementation experiments of Stotzky and Norman (1961b) sulfur limitation became evident once the N and P requirements had been met in a soil amended to 4% glucose. For natural situations, only microzones surrounding a plant root would ever attain such a high carbon substrate level. Thus, nutrient limitation may not be apparent in general. The reported result does indicate that fertilization can be beneficial if C is not limiting, as for instance in oil remediation efforts, or when high levels of carbonaceous contaminant are applied to nutrient poor soils.

Christensen et al (1994) recently reviewed attenuation of landfill leachate pollutants in aquifers and concluded that complete natural attenuation of organic materials commonly occurs within one km from the landfill, at least for sandy/gravelly aquifers. In this situation, vegetation may pump contaminated water from shallow aquifers through evaportranspiration. Leachate chloride ion was used as a natural, conservative tracer. Part of the maintenance energy to sustain microbial populations is likely to come from plant exudates, but in some zones, redox chemistry of mineral elements may be quite significant. Christensen et al (1994) described several zones of different redox level at different distances from the leachate source. Plants generally would contribute in a direct way only to the more oxidized zone. There is no report of comparative attenuation rates in vegetated vs unvegetated settings.

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3.2. Plant contribution and bioenergetics

If a plant is to directly remediate significant concentrations of contaminant, it must carry out a degradative reaction, rather than simply sequestering the contaminant as something such as a glucose conjugate. This follows from basic energetic considerations. Typical higher plants using C-3 photosynthesis take up about 500 mL water for each gram of dry matter produced, although C-4 pathway plants may be twice as efficient. If a contaminant is present at 1 mM and must be conjugated to glucose for sequestration, each mmol of contaminant taken up will be linked with production of about 2 g dry matter, or roughly 10 mmol glucose equivalent. Thus 1/10 of the primary photosynthate must be dedicated directly to sequestering the contaminant in the simple case of conjugation to glucose. A further portion must be associated with production of structures into which the conjugate may be stored. For a compound such as toluene with a molecular weight of about 100, a 1 mM solution is 100 mg/L. When plants are grown on water containing 500 mg/L toluene as we have done, nearly all their photosynthetic capacity would have to be dedicated to sequestering it, if that were the only mechanism for its disappearance. We have done extensive studies with toluene supplied at this level (c.f. Muralidharan et al, 1995b) and do not find growth inhibition. The contaminant does not appear to leave the ground via volatilization (Davis et al, 1994) so it presumably does not enter the plant in large quantities. For toluene, degradation appears to take place within the vadose zone or rhizosphere.

For other contaminants the energetic argument is somewhat more complex but the essential point is the same. For instance, atrazine is sequestered in maize by conjugation to a much more complex compound than glucose (Shimabukuro, 1968), one which undoubtedly uses much more energy to produce per mole than glucose. So there is a limit to the levels of atrazine

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that could be processed by a maize plant without reduction in its overall growth, independent of any herbicidal effects that might be induced. Trinitrotoluene is another compound which probably must be metabolized, not just conjugated (Mueller et al, 1993), in order to effect successful remediation. However, both atrazine and trinitrotoluene would supply the maize plant with "excess" nitrogen if extensively metabolized from an initial input of 3 mM external solution. Hence, even genetically engineered tolerance will experience significant constraints in the cleanup capabilities of the plants themselves.

For some compounds such as highly chlorinated hydrocarbons, there is insufficient energy released during their oxidation to allow growth of microbes (Vogel et al, 1987) or presumably plants. They are good electron acceptors, not donors. Consequently, successful remediation usually depends on cometabolism or gratuitous metabolism. A recent review of biological treatment methods for halogenated hydrocarbons (Murray and Richardson, 1993) describes the diversity of pathways that are available for remediation. For instance, aromatic compounds such as toluene, benzene and xylenes (BTEX) are commonly degraded by oxidative pathways. Fan and Scow (1993) showed that toluene or phenol can induce indigenous microbial populations to degrade TCE. Similarly, naturally occurring plant phenolics might also.

Methane mono-oxygenase or alkene mono-oxygenases, which have as their primary substrate methane or an alkene, are able to oxidize TCE in a fortuitous reaction (Ensign et al, 1992, Ewers et al, 1990). Plants obviously do not supply methane directly but transfer exudates to anaerobic sites which may allow methane formation. The methane may then be used by methanotrophs after passing to a zone where oxidant is available (Davis et al, 1994).

When oxygen is insufficient to sustain respiration, another electron acceptor, such as nitrate or sulfate, may serve in a similar role for degradation of many organic compounds found in landfill leachates (Christensen et al, 1994). Sulfate reduction may be an alternative or co-existent with methanogenesis according to their studies.

For reductive dechlorination, which is another possible route to degradation of TCE (Vogel et al, 1987), a supply of reductant is required. This may be supplied, as in the studies of Christensen et al (1994), by pathways that yield sulfide or methane. The general equation given by them for methane formation is $2CH_2O \rightarrow CH_3COOH \rightarrow CH_4 + CO_2$. Plants are (ultimately) the most likely source of CH_2O even in landfill leachates. Contaminants that have a low energy yield, or that are present in low concentration, may not be efficiently degraded by microbes because the population (number) of capable bacteria is too low to perform the job in a reasonable time or the affinity of degradative enzymes for the contaminant as substrate is too poor to remove the last traces of a compound in a reasonable time. The added energy input from plant-supplied CH_2O provides maintenance energy requirements for a larger microbial population, which in turn helps drive the contaminant concentration to zero (Erickson et al, 1994a,b, 1995).

A plant growth system maintained in the laboratory showed both production and disappearance of methane when ground water containing both TCE and TCA was supplied continuously. The system, which has been described in detail (Davis et al, 1994, Muralidharan et al, 1995a), consists of a channel 10 cm wide, 35 cm deep and 1.8 m long planted with alfalfa. The groundwater supplied was saturated with oxygen. Methane production occurred only in the 2nd half of the flow path, presumably after consumption of available oxygen in oxidation of

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available carbon substrates. Although methane appeared in the ground water, it did not appear in the gas phase above the plants (Muralidharan et al, 1995a, Visser et al, 1994). Presumably methanotrophs in the vadose zone consumed it as an oxidizable energy source. Methane monooxygenase may well have fortuitously degraded some of the TCE, although it is difficult to pinpoint the exact sites of TCE disappearance. Release of chloride in the ground water outflow indicated that a portion of chlorinated hydrocarbon was being degraded in ground water, while accumulation of chloride in the soil at the top of the chamber indicated further dechlorination. These two processes were estimated to account for about 17% of TCE which disappeared (Muralidharan et al, 1995a). These experiments were done with rather high levels of TCE (200 μL/L input to ground water). Such high levels may have taxed the capacity of plants to supply co-substrate for support of a microbial flora. Even so, passage of ground water through a longer region should have led to further, possibly complete degradation. High input levels were used both for analytical convenience and to demonstrate tolerance of a plant-based system for the presence of a potentially toxic contaminant.

4. Unique status of the rhizosphere

As discussed in the work of Anderson et al (1993), the rhizosphere frequently supports the presence of consortia of microbes that are able to degrade compounds even though individual species cannot, despite supplementation with energy sources. We understand too little of rhizosphere dynamics to fully explain such a phenomenon but it presumably involves cross-feeding between organisms. The plant contributes both simple and complex C and N sources for use by several microbes that in turn may release partial degradation products usable by other

species. Other important contributions may include vitamins, pH alterations in microsites, and metal solubilization or complexation.

The rhizosphere is a zone with microbial biomass present at a much higher level than in bulk soil. Most commonly, increase of biomass is determined by measuring numbers of culturable organisms. However, mycorrhizal fungi that specifically colonize plant roots, may not increase greatly in numbers, while still increasing greatly in biomass. It is difficult to determine the number of organisms represented by a mycelial mat, whereas bacterial counting is more straight forward. Mycorrhizal fungi may degrade complex aromatics (Anderson et al, 1993). Other fungi, commonly associated with decaying roots, are well known for their abilities to degrade a diversity of aromatics including trinitrotoluene (Majcherczyk et al, 1994).

5. Plants as pumps

An important consideration in vegetative remediation strategies is the extent to which plants can contain contaminant plumes and enhance transfer of contaminated ground water into the metabolically more active vadose zone and the rhizosphere. Much work has been done studying transpiration mechanisms in single leaves or plants. There are fewer measured values of transpirational losses over long time periods for entire stands or groups of single species of trees, or crops such as alfalfa, and even fewer for plants such as prairie grasses. For large areas such as watersheds, one can calculate apparent transpiration from measurements of precipitation minus interception, soil evaporation and runoff. This measured value does not necessarily indicate the upper bound of potential evapotranspiration (Pet) for well watered conditions. We discuss the meaning of Pet more extensively below. It has been defined in operational terms as

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the amount of water used by a short crop of uniform height, completely shading the ground and grown under well watered conditions (Penman, 1967).

Forests and fields are frequently water or nutrient limited. They may well use different amounts of water depending on their response to transient stresses that vary from year to year. Dominant members of the flora may also have a determinate growth habit so that for part of the year they are relatively inactive. For instance, shoot growth of pine trees responds to water availability at a critical stage of growth, rather than throughout the entire year. Indeterminate growers like eastern red cedar, cottonwood, willow or grasses may respond to water availability by a new growth spurt, once a water stress is removed. Phreatophytes (plants that can extend their roots into the water table or capillary fringe) may use much larger amounts of water, as do cottonwoods along desert streams, than does the bulk of vegetation in a typical forest stand or prairie grassland (Robinson, 1958). However, the apparent extent of obvious aboveground growth does not necessarily indicate total photosynthesis or transpiration rate of a plant. Actual measurements are needed for estimating net transfer of photosynthate to the rhizosphere, but are generally unavailable. Belowground production may be quite significant for prairie grasses or deep-rooted trees. For water use, there are some measurements available. They are cited below.

Maximizing the amount of water pumped by plants to contain a contaminant plume may be contrary to the goals of most crop producers who are seeking to optimize water use efficiency. Alfalfa, which is usually stated to have a poor water use efficiency (Black, 1971), may store quite a large biomass belowground. Depending on climatic conditions, alfalfa may also have a measured water use efficiency quite comparable to other crops. In southwestern

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Kansas, hay production with measured amounts of water input is 1.87 g per liter water used for a full season (Kansas AES, 1992). For better cultivars, the yield is 10% greater.

It is hard to find data expressed, or experiments designed, in terms useful for the present calculations. For watersheds in the western U.S., a recent annotated bibliography (Johns, 1989) serves as a convenient source of abstracts indicating relative rates of water usage by different species. The emphasis of the book is on natural rather than planted vegetation so there is a strong bias toward certain species and against others. Some of the cited values are suspect because they are derived on the basis of assumptions that may not be generally applicable, but they do give a reasonable indication of potential water use. Cattails, cottonwoods, rushes, reeds, sedges and tamarix are all reported to exceed 60" (150 cm) water use per year in some locations, though not all. Most of the high values were observed in the southwestern U.S. where the Pet may be quite large. In the U.S., Pet equals or exceeds precipitation throughout the corn belt and central Great Plains. Further east and south, supply and demand are, on average, closely matched (Kozlowski et al, 1991), so that one may safely assume that Pet approximates the rainfall for the area ± 15%.

5.1. Estimating rates of transpiration

An estimate of transpirational losses can be made for crop plants, based on energy inputs, working from the principle that the energy of vaporization of water is the common denominator of evaporative and transpirational processes. Penman (1948) made a thorough analysis and derived an estimating equation that appeared reasonably accurate over a number of different climates (Penman, 1967), although it was developed in a temperate European setting. Baumgartner (1967) calculated that forests use about 30% more water than field crops such as

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alfalfa, on the basis of energy balance studies in Germany. Bare soil loses the least water because of its reflectivity and self-mulching of the loose surface layer.

In a detailed analysis of transpiration measurements made over a number of years at a range of locations in the U.S., Jensen and Haise (1963) developed simple formulas to predict Pet based on solar inputs and temperature. Tanner (1968) discussed the relative merits of several different approaches to estimate Pet. In discussion below, we will use the term Set to describe the energetically estimated potential evapotranspiration term that is independent of temperature. This was called R_s by Jensen and Haise (1963) and tabulated for all seasons of the year for several latitudes at sites with varying extents of cloud cover. Depending on the environment, factors such as wind velocity (Skidmore et al, 1969) or reradiation of stored heat may be significant. All incoming radiation has to go somewhere. Very little, from 1-3 %, is used for photosynthesis, and the rest either is stored, re-emitted or evaporates water (Tanner, 1968). Typically two-thirds of incoming radiation is used to evaporate water (Cowan and Milthorpe, 1968).

For an extensive area under consideration, for example one hectare, edge effects are minimal. Over periods of days to weeks, fluctuations in net energy input are averaged. Hence, energy balance methods work well so long as water is not extremely limiting. Obviously, desert cottonwoods along streams transpire much more than calculated directly from solar inputs because there is a large heat flux from the surroundings, and significant advection. For purposes of modeling remediation, the assumption of a large areal extent of the planted site is therefore a conservative assumption. Unless the canopy is fully closed and the soil is mulched, there will be some evaporation which also assists in bringing water to the surface.

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Surface roughness affects water use. Trees provide a rougher surface than alfalfa or grasses and so they lose more water at the same wind velocity and average relative humidity (Baumgartner, 1967, Rutter, 1968, Sopper and Lull, 1967). For a given roughness, increasing wind velocity from 2 m/sec to 6 m/sec increases Pet from 0.98 of energy balance expectation to 1.6 times (Skidmore et al, 1969). The latter wind velocity is only 22 km/hr which is the monthly average wind velocity in many parts of Kansas and throughout the Great Plains. Thus, one could have a water usage greater than the Set, if plants did not respond defensively to such stresses by shutting down their stomates. However, they do so and, as shown below, it is only in rare situations that one finds actual water use to exceed Set over any substantial interval.

The sum of evaporation and transpiration from typical crops over drier portions of the country must certainly be less than the potential evapotranspiration (Pet) derived from the energy balance and temperature for those sites, unless irrigation is provided. For instance, at Dodge City in southwestern Kansas, Set is about 112 inches (285 cm) per year (Jensen and Haise, 1963), while rainfall is less than 20" (50 cm). Nearly 90" of Set comes from April to October. Most crop species only cover the land for a portion of the season and grow actively for a few months. An evergreen, nondeterminate crop in a mild climate could approach the annual Set amount of water if it were available, so that the Pet (Penman, 1948) might approach Set. Alfalfa or hybrid poplars may realistically use at least half to two-thirds the Set over the course of their active growing season, which may extend over 6 months or more in mild climate. Because trees provide a rougher surface, tall indeterminate growers such as poplars may occasionally in some seasons even exceed the predicted amount based on Set, because they "capture" heat energy brought by the wind from unvegetated areas. This is especially the case

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for small areas -- the oasis effect which may be important for effective plant-based pumping of contaminated ground water, whereby a moderate sized stand of trees serves to contain a spill.

Further north and east where cloud and aerosol levels in the atmosphere are increased, and growing season is decreased by cold, the Set is less than in clear climates and the typically used fraction is much less (Jensen and Haise, 1963). For Stillwater, OK, the annual Set is about 100 inches, with 80" Set from March to October. At Bismarck, ND, the Set is 94" with 64" from April to September. By contrast, at Phoenix, AZ, annual Set is 128" (3.2 m), and climate is hot enough that year round water use may approach Set.

At Prosser, WA, in a temperate climate, an alfalfa crop transpired two-thirds of the Pet over most of the season. In Arizona, the ratio of Actual/Potential increased for alfalfa as a function of temperature such that it approached a ratio of 1 at a mean daily air temperature of 27°C. Similar results were found for other crops at other locations (Jensen and Haise, 1963). So, for identical crops in cooler climates, the fraction of Set used would be less than it would be in hotter climates. The equation describing this relationship was given as

$$Et/Set = 0.014T - 0.37,$$

where T was given in °F. We may rewrite the equation as

$$Et/Set = 0.0252T + 0.078$$

to express T in °C. At a mean air temperature of 5°C, actual Et is only about 1/5 Set. This relationship was later fitted to a study in Davis, CA, of rye grass, which represents Penman's ideal crop, with good results (Jensen and Haise, 1963).

Data in the thesis of Licht (1990) allow estimation of water use of hybrid poplars. At Amana, IA, he observed aboveground biomass accumulation of 3 kg/m² in one season, and in

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greenhouse studies of trees grown in large tanks, water usage was about 0.6 L/g biomass. This would translate to a water use of 1.8 m depth per season for field grown trees, assuming comparable water use efficiency. For a C-3 type plant, such a water use efficiency is quite reasonable (c.f. data of Shantz and Piemeisel cited by C.C. Black, 1971).

Eucalyptus plantations in Australia are reported as using 2.3 m water per year from interception and transpiration, when rainfall is only 0.68 m (Greenwood et al, 1985). The surrounding pasture may use $\cong$ 0.4 m. Eucalyptus have been used to drain swampy areas (Calder, 1992).

Some *Tamarix* species are reported to use over 2 m/yr when the water table is held at 1.5 m, but only 1 m when it is at a depth of nearly 3 m (van Hylckama, 1970, 1974). This study was done in a large stand of trees at Buckeye, AZ, where Set is even larger than at Phoenix, AZ. One may thus observe that trees, in a large stand, still did not exceed the Set for the site (>3 m/yr), even when the water table was very shallow.

Perhaps the most extreme situation is the well documented study of McDonald and Hughes (1968), conducted near Yuma, AZ. In lysimeters with a controlled water table, cattails with water at the surface used 100" per year (2.5 m) while bermuda grass with a 3.5 ft (1.25 m) deep water table used 73" (1.9 m). This indicates that one need not depend on what are usually classified as phreatophytes to obtain large water usage. Bermuda grass is both drought resistant and water-consuming. One must design with consideration of the actual water table and response of the plant species to water availability. Irrigation with contaminated water may enhance plume control and crop production.

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Single trees growing in isolation under ideal conditions might consistently exceed Set by as much as 50% but a significant sized stand is unlikely to do so. A plant subjected to extremes of wind or other energy transfer necessary to exceed Set is unlikely to do so for long periods of time. It will adapt to water stress by conservation measures such as closure of stomates. Thus, water usage is probably not going to exceed 2-3 m per year in most parts of the world, as shown above. However, at this level, for 7 ft water use per year (2.2 m) with a contaminant concentration of 1 ppm, about 18 lb per acre per year (22 kg/ha) of contaminant could be taken up into the plant if the TSCF (partitioning of contaminant into the transpiration stream) were 1.0. This is a factor of five fold lower than the interesting but overly optimistic estimate of Stomp et al (1994). However, it is still a significant amount of material.

5.2. Depth of soil water depletion

The above analysis indicates that appropriately chosen vegetation may pump considerable amounts of water, and allows reliable estimation of likely water usage as a function of climate for plume management. Use of 1 m of water will lower the water table in an enclosed area by 3-10 m, depending on soil porosity. Recharge of the soil will depend on available sources and permeability. For a sandy soil along a river, such as our local landfill in Manhattan, KS, trees are unlikely to lower the water table very much over a year because recharge can occur at night and during their dormant period. For a lower permeability soil in a low rainfall area, they can lead to quite appreciable depression of the average water table. It has been reported that diurnal variations in water tables can be measured under alfalfa and other plants (White, 1932). For instance, in the Utah desert with alfalfa, the maximum daily fluctuation was over 6 cm, rising at night and declining by day. This water fluctuation could assist mass transfer of air into the

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soil. In poorly drained soils, there may be marked annual variations in the water table. Holstener-Jorgensen (1967) measured seasonal changes greater than 1 m in Denmark.

Shachoris et al (1967) examined water profiles in a Mediterranean karst soil, in Israel, under different vegetation types. Below scrub shrubs, water withdrawal was to a depth of 8 m of the soil column, while it was only 2-3 m under pasture grass. Drought tolerant species are well known to withdraw water from considerable depths. Typical tree and crop species have most roots in the top 1 m of soil although desert shrubs may have some roots many meters deep and prairie grasses extend at least a few roots down several meters (Shimp et al, 1993).

For alfalfa, distribution of roots within the soil column was uninfluenced by frequency of irrigation (2 -12 times per year) over several years when the total annual amount was kept constant (Stanberry, 1955). Two thirds of the roots were within the top half meter, but root activity in water abstraction obviously varied with water availability. With few but deep irrigations, much more of the water was withdrawn from greater depths by the fewer roots present at those depths.

As mentioned above for *Tamarix* spp., their water usage varied markedly with depth to the water table. Some species are able in this way to limit both their growth and their water usage, and can survive on much less than optimal amounts of water. This flexibility can be an advantage if one wishes to maintain a water table at a reasonable depth.

5.3. Possibilities of intermedia transfer

As discussed in Shimp et al (1993) and Trapp and McFarlane (1995), the amount of contaminant transferred through a plant depends on the transpiration stream concentration factor (TSCF) which reflects relative solubility of the contaminant in water and lipid. Materials that

are about 100 x more soluble in octanol than water, i.e. with a log K_{ow} of 2, generally have a TSCF approaching 0.8 (Briggs et al, 1982). More, or less, polar compounds have a lesser ability to move into the plant, either because they cannot pass through membranes or because they are too water insoluble (Trapp and McFarlane, 1995). Most PAHs cannot move appreciably into plants from soil and remediation depends almost totally on rhizosphere microbes. Typical herbicides and pesticides were designed to have optimum mobility characteristics and typically are relatively non-volatile, so they either accumulate in or are metabolized by plants.

Low molecular weight chlorinated hydrocarbons like TCE have relatively high TSCF values but are also volatile and can potentially leave the plant unchanged, by volatilization from the leaves. With the most active plausible transpiration rate of 1 cm/day (10 L/m^2) based on energy input estimates, TCE could be transferred to the atmosphere at 10 g/m^2/day, given a water solubility of TCE around 1.5 g/L and a TSCF of 0.67 (estimated from equation of Briggs et al, 1982). On a relatively calm day in Kansas with a wind speed of 3 m/s, 10 g ($\sim 1/13$ mol or 2 L gas) would be dispersed into 2.6 x 10^6 cubic meters of air assuming mixing into only the lowest 10 m of the air column. More realistic ground water concentrations, say 1-15 mg/L, and greater mixing height of 100-300 m would give a concentration 10^4-10^6 lower. Hence, even a rather large contaminated area of 1 ha would only give a low air concentration downwind under a worst case scenario of intermedia pollutant transfer.

Another way to consider the problem is to recognize that water is only "soluble" in air to the extent of about 30 mg/L at 30°C. As a consequence, any dissolved compound that is transferred to air by transpiration through a plant must undergo a minimum of a 1/33,000 fold dilution. More typically, the relative water vapor pressure deficit is smaller than this and air

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in transit over a leaf does not become water saturated. Hence the dilution from water to air may be more like 10^5 fold or greater. Very few contaminants are sufficiently water soluble, non-toxic to plants, and volatile enough to reach atmospheric concentrations that would be of concern when dispersed by this mechanism. Exceptions might be freons or related substances.

Measured values of contaminant concentrations in the gas phase have been made using Fourier Transform Infra Red (FTIR) instrumentation in a closed laboratory chamber (Davis et al, 1994, Muralidharan et al, 1995a). Carbon dioxide production can also be measured readily. In an open laboratory chamber, gas phase concentrations of contaminants are so low that detection is difficult.

6. Water application and remediation

Thus far, the discussion has assumed that plants are obtaining water strictly from the ground with a variable input from precipitation. In some situations, it might be advantageous to use plants as a low cost "pump and treat" remediation system. Fields of plants, supplied with water through irrigation, may be used to biodegrade contaminants in the rhizosphere. When dealing with non-volatile materials, a constructed wetland may be the most economical and effective approach to use. There are a number of books on the subject as cited by Shimp et al (1993). A recent article in *American Scientist* (Jewell, 1994) provides an excellent introduction to constructed wetlands for wastewater purification. The standard method is a free surface water wetland but more recently, nutrient film and subsurface-flow designs have proven highly effective. In most climates, water loss from open water is somewhat greater than from a planted crop. However, if there is a considerable amount of non-living plant matter sheltering the water surface, losses may be lower than for planted land (Idso, 1981). That is why in arid climates,

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water loss from phreatophytes or hydrophytes such as cattails growing in a lake may be large but still not exceed Pet for that environment.

Intermedia transfer of volatiles may be a problem when there is a free surface water system (with mixing). However, it is unlikely to be a problem following transpiration through a plant because release of contaminant is linked to water loss. Consequently, construction of a subsurface drip irrigation system for remediation of dissolved organics is feasible. There are no published reports on this approach with plants, but two papers in a recent publication (Hinchee et al, 1994) deal with the concepts involved in more general bioremediation configurations.

Allen-King et al (1994) applied a mixed organic (gasoline) contaminated water to soil that had recently been cleared of plants, and hence was a rhizosphere soil. It was a relatively undeveloped sandy soil with a high porosity. A natural column was isolated by driving a 91 cm diameter pipe 2.3 m into the ground (to the water table). A large fraction of the applied amount of BTEX was removed in the upper layers, until degradative capacity of the soil was exceeded. The application rate was high, 32 mL water /cm²/d at an input concentration of 7 mg/L BTEX. A comparable experiment was done on a 5 m x 5 m plot using drip irrigation equipment, with emitters laid on the soil surface. In this instance, water application rate was 58 mL/ cm²/d at 9.7 mg/L of BTEX. It was calculated that only a small percentage of BTEX was lost through volatilization. Addition of ammonium nitrate greatly enhanced performance of the system which was apparently nitrogen limited ($NH_4^+ + NO_3 < 10$ mg/kg). Such high water application rates would not be possible, except with a very porous soil, so the method is not generally applicable. Plant consumption of water per surface area would be only about 1% of this rate. The system

described is actually an effective sand filter with an indigenous population of microbes. To use plants, such a system would need to be much more extensive in area, or operate at a lower rate of water abstraction.

Baker et al (1994) designed a vadose zone column to test treatability of organics by soil venting. Tracer ^{14}C toluene was applied one time only in water solution along with ethyl benzene and xylenes. Air entered 5 cm and departed 25 cm below the soil surface in a pyrex column. Essentially no label left the air above the column and little was recovered unchanged at the end of the experiment. About one-fourth was mineralized. Adding a low level of nitrogen fertilizer slightly enhanced mineralization but a higher level inhibited it. This experiment and the one cited above indicate potential for pump and treat approaches. A plant-based system would have a clear advantage if soil porosity were so low that unhindered water movement was very low, or if plants could be used to supply needed N or other nutrients to enhance mineralization of contaminants. The plants might also supply a product of value from the remediation process, recovering part of the input expenditures.

7. Model for plant-based remediation

A model for plant-based bioremediation which has been developed by this group visualized the root-soil environment with transpiring plants as a porous medium comprised of soil particles and soils which may be partially or fully saturated. Below the water table, the soil is fully saturated with water, while in the vadose zone, where the root zone of plants is often present, water and gas phases are both present. The rhizosphere, or the root influence zone, surrounding the plant roots may extend as far as one to six meters deep in the soil depending on vegetation and depth of the water table at the site. Alfalfa plants and poplars are known to

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generally extend their roots down to approach even a deep water table. During wet climatic or high water table conditions, interparticular voids of the soil matrix may be predominantly filled with water. In relatively dry conditions, especially in summer when there is a higher evapotranspiration rate, a greater fraction of voids may be occupied by the gas phase. During phytoremediation, transpiring vegetation may contribute to movement of water up from the subsurface region, hence lowering the water table (Shimp et al, 1993, Erickson et al, 1994b). Vegetation could therefore increase the depth of the unsaturated zone and consequently help to increase oxygen transfer in gas-occupied voids (Shimp et al, 1993, Erickson et al, 1994b). Basically, in the saturated zone, water content, θ, is equal to the soil porosity (interparticular voids); that is,

$$\theta = \eta \qquad (1)$$

and in the unsaturated zone, the void fraction, θ_a, occupied by the gas phase is,

$$\theta_a = \eta - \theta \qquad (2)$$

Various constituents simulated in the subsurface environment are the contaminant, microbial biomass, oxygen, and root exudates. The model incorporates a number of physical, chemical, and plant-related phenomena associated with fate and transport processes of these components in porous media. Physical transport of these components during water flow includes advection and dispersion phenomena in two dimensions. Advection includes ground water convective flux which can be modeled based on the site's hydrogeologic survey. Dispersive transport of ground water is primarily assumed to be due to mechanical dispersion in the subsurface environment. Dispersion in the horizontal direction is along the ground water flow

path and in the vertical direction is associated with precipitation and evapotranspiration processes.

Physical processes are assumed to include sorption, volatilization, and gas phase diffusion through void spaces. Sorption is a significant phenomenon when considering bioremediation of hydrocarbon compounds. Sorption of contaminants, biomass, and exudates may occur onto either the soil particle surface or root surface in the rhizosphere soil. Volatilization plays a major role in the disappearance of compounds when dealing with bioremediation of volatile organics. Gas phase diffusion of contaminants occurs in the upward direction through gas-occupied voids of the soil, whereas diffusion of oxygen occurs downwards from the atmosphere into the surface soil.

7.1. Plant-related phenomena

Bioremediation involving plants is significantly influenced by precipitation and evapotranspiration which results in vertical movement of the soil-water due to pressure gradients. Upward transport of ground water also results in the upward movement of dissolved components along with soil water to the rhizosphere of plants (Davis et al, 1993, Shimp et al, 1993, Erickson et al, 1994b). Therefore, the model incorporates a term for the uptake of water and various components dissolved in the ground water of the aquifer. Most importantly, the model includes the process of uptake of the contaminant by vegetation. The extent of uptake of the contaminant by roots and shoots is modeled using RCF (Root Concentration Factor) and TSCF (Transpiration Stream Concentration Factor) coefficients, respectively. The RCF and TSCF coefficients are determined using log K_{ow} (Octanol-Water partition coefficient) values of the

organics, which are tabulated in the literature. Equations relating RCF, TSCF, and log K_{ow} used in the model were developed by Briggs et al (1982) and are shown below:

$$R_{CF} = 0.82 + 10^{(0.77 \log K_{ow} - 1.52)} \tag{3}$$

$$T_{SCF} = 0.784 \exp\left(- \frac{(\log K_{ow} - 1.78)^2}{2.44} \right) \tag{4}$$

Rhizodeposition and root exudation of carbon enriched substrates by plants occur in the root-soil environment. Plants such as bald cypress, cottonwood, and willow are known to also supply oxygen through the roots to the subsurface soil environment (Shimp et al, 1993). The extent of loading exudates (Q_r) and oxygen (Q_o) into the root-soil environment is usually dependent upon the root density factor (R_d) in the rhizosphere of the plant. The higher the R_d, the more eutrophic the root-soil environment may be during the phytoremediation strategy. The R_d factor varies according to soil moisture and nutrient conditions, but generally decreases exponentially with depth in the soil profile (Tracy et al, 1993, Tracy et al, 1994).

7.2. Microbial kinetics

Rhizosphere soil supports a higher population of biomass due to increased availability of nutrients in the form of root exudates. Root exudates contain a variety of carbon compounds such as carbohydrates, vitamins, and amino acids which may act as essential growth enhancers for microbial populations. Oxygen is important for proliferation of aerobic microorganisms (Lee et al, 1988). Rhizosphere soil is mostly in the vadose zone and generally harbors aerobic microorganisms (Davis et al, 1993, Shimp et al, 1993, Erickson et al 1994b) that are dependent

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on carbon and oxygen for their growth and energy requirements. In this model, these two substrates are assumed to limit growth of the microorganisms according to a two-substrate Monod kinetic model which is presented below.

7.3. Model equations

Mass balances for components in an aquifer element that is representative of a contaminated root-soil environment leads to Equations (5)-(8) where words are printed above each term to clarify the equations. Equation (5) assumes that only one contaminant (C) is prevalent in the groundwater in dissolved form and that it is not present as non-aqueous phase liquid blobs. The contaminant will be present in the liquid phase, gas phase (depending on the vapor pressure), plant phase, or on the soil particles and root mass surfaces. Contaminant concentration may be appreciable in the gas phase if the contaminant is volatile. Adsorption is incorporated to account for presence of contaminant on soil and root surfaces. Microbial degradation of the contaminant is expressed using the Monod two-substrate model. The mass balance for the contaminant is

Rate of change in contaminant concentration　　Plant uptake

$$\frac{\partial}{\partial t}\left[C\left(\theta + R_d R_{CF} + \rho K_{ds} + \theta_a H_s\right)\right] = -qT_{SCF}C$$

Contaminant transport in horizontal direction

$$+ \frac{\partial}{\partial x}\left[\theta\left(D_{xx}\frac{\partial C}{\partial x} + D_{xz}\frac{\partial C}{\partial z}\right) + \theta_a H_s\left(D_{as}\frac{\partial C}{\partial x} + D_{as}\frac{\partial C}{\partial z}\right) - V_x C\right]$$

Contaminant transport in vertical direction

$$+ \frac{\partial}{\partial z} \left[\theta \left(D_{zx} \frac{\partial C}{\partial x} + D_{zz} \frac{\partial C}{\partial z} \right) + \theta_a H_s \left(D_{as} \frac{\partial C}{\partial x} + D_{as} \frac{\partial C}{\partial z} \right) - V_z C \right]$$

Contaminant degradation in biomass

$$- \left(\frac{\mu_m}{Y_s} \right) (\theta + R_d R_b + \rho K_{db}) C_b \left[\frac{C}{(K_{rs} + C + C_r)} \left(\frac{C_o}{K_o + C_o} \right) \right] \qquad (5)$$

A microbial mass balance was similarly performed by considering the presence of the microbes (C_b) in the aqueous phase, on the soil particles, and on root mass surfaces. Microbial growth was considered to occur with contaminant, exudates, and oxygen available in the soil. Equation (6) is the balance for the microbial mass in the root-soil environment.

Rate of change in biomass concentration $\qquad\qquad$ Biomass transport in horizontal direction

$$\frac{\partial}{\partial t} \left[C_b (\theta + R_d R_b + \rho K_{db}) \right] = \frac{\partial}{\partial x} \left[\theta \left(D_{xx} \frac{\partial C_b}{\partial x} + D_{xz} \frac{\partial C_b}{\partial z} \right) - V_x C_b \right]$$

Biomass transport in vertical direction $\qquad\qquad$ Biomass decay

$$+ \frac{\partial}{\partial z} \left[\theta \left(D_{zx} \frac{\partial C_b}{\partial x} + D_{zz} \frac{\partial C_b}{\partial z} \right) - V_z C_b \right] - k_d (\theta + R_d R_b + \rho K_{db}) C_b$$

Biomass growth

$$+ \mu_m (\theta + R_d R_b + \rho K_{db}) C_b \left[\frac{C + C_r}{(K_{rs} + C + C_r)} \left(\frac{C_o}{K_o + C_o} \right) \right] \qquad (6)$$

Similar balances are shown in Eqs. (7) and (8) for oxygen (C_o) and root exudates (C_r) present in the root zone of the plant.

Rate of change in   Oxygen
oxygen concentration   loading   Plant uptake

$$\frac{\partial}{\partial t}\left[C_o \left(\theta + \theta_a H_o \right) \right] = q_o C_{or} - q T_{scfo} C_o$$

Oxygen transport in horizontal direction

$$+ \frac{\partial}{\partial x}\left[\theta \left(D_{xx}\frac{\partial C_o}{\partial x} + D_{xz}\frac{\partial C_o}{\partial z} \right) + \theta_a H_o \left(D_{ao}\frac{\partial C_o}{\partial x} + D_{ao}\frac{\partial C_o}{\partial z} \right) - V_x C_o \right]$$

Oxygen transport in vertical direction

$$+ \frac{\partial}{\partial z}\left[\theta \left(D_{zx}\frac{\partial C_o}{\partial x} + D_{zz}\frac{\partial C_o}{\partial z} \right) + \theta_a H_o \left(D_{ao}\frac{\partial C_o}{\partial x} + D_{ao}\frac{\partial C_o}{\partial z} \right) - V_z C_o \right]$$

Oxygen consumption by biomass

$$- \left(\frac{\mu_m}{Y_o} \right) \left(\theta + R_d R_b + \rho K_{db} \right) C_b \left[\frac{C + C_r}{(K_{rs} + C + C_r)} \left(\frac{C_o}{K_o + C_o} \right) \right] \qquad (7)$$

Rate of change in exudate concentration   Exudate   Plant uptake
                                               loading

$$\frac{\partial}{\partial t}\left[C_r \left(\theta + R_d R_r + \rho K_{dr} + \theta_a H_r \right) \right] = q_r C_{rr} - q T_{scfr} C_r$$

Exudate transport in horizontal direction

$$+ \frac{\partial}{\partial x}\left[\theta \left(D_{xx}\frac{\partial C_r}{\partial x} + D_{xz}\frac{\partial C_r}{\partial z} \right) + \theta_a H_r \left(D_{ar}\frac{\partial C_r}{\partial x} + D_{ar}\frac{\partial C_r}{\partial z} \right) - V_x C_r \right]$$

Exudate transport in the vertical direction

$$+ \frac{\partial}{\partial z} \left[\theta \left(D_{zx} \frac{\partial C_r}{\partial x} + D_{zz} \frac{\partial C_r}{\partial z} \right) + \theta_a H_r \left(D_{ar} \frac{\partial C_r}{\partial x} + D_{ar} \frac{\partial C_r}{\partial z} \right) - V_z C_r \right]$$

Exudate consumption by biomass

$$- \left(\frac{\mu_m}{Y_r} \right) (\theta + R_d R_b + \rho K_{db}) \, C_b \left[\frac{C_r}{(K_{rs} + C + C_r)} \left(\frac{C_o}{K_o + C_o} \right) \right] \qquad (8)$$

Equations (5)-(8), which are used to describe biodegradation of a contaminant in the root zone of growing plants, are called the contaminant fate model equations. In these equations soil-water fluxes (V_i), soil-water content (θ), and dispersion coefficients (D_{ij}) are computed prior to solving Eqs. (5)-(8). Darcy's soil-water fluxes (V_i), soil-water content (θ), hydraulic conductivities (K_{si}), and dispersion coefficients (D_{ij}) are evaluated based on soil-water pressure head (ψ_s) using soil characteristic Equations (9)-(12).

$$V_i = -K_{si} \left(\frac{\partial}{\partial x_i} (\psi_s + z) \right) \qquad (9)$$

where $x_1 = x$ and $x_2 = z$. Darcy's soil-water fluxes $(V_1 = V_x$ and $V_2 = V_z)$ can then be used as advective transport parameters in Eqs. (5)-(8). Soil-water content (θ) is a function of soil-water pressure head (ψ_s), and can be simulated using Brutsaert's equation (Brutsaert, 1966)

$$\frac{\theta}{\eta} = \frac{A}{A + (-\psi_s)^c} = S_e \qquad (10)$$

Hydraulic conductivity depends on soil-water content; it can be simulated using the model of Brooks and Corey (1966)

$$K_s = K_{sat} \left(\frac{\theta}{\eta}\right)^d \qquad (11)$$

In Equations (10) and (11), A, c, and d are soil characteristic parameters.

The hydrodynamic dispersion term D_{ij} is calculated based on Darcy's soil-water fluxes (V_i) and dispersivity factors (α_i) which are characteristic of the soil utilized for simulation in the respective directions, resulting in

$$\theta D_{ij} = \alpha_i |V| \delta_{ij} + (\alpha_i - \alpha_j) (V_i V_j / |V|) \qquad (12)$$

In order to obtain θ, V_i, D_{ij}, and K_s using Eqs. (9)-(12), one has to know the soil-water pressure head (ψ_s) distribution. In a bioremediation strategy involving plants, ψ_s will be significantly influenced by the evapotranspiration phenomenon. Essentially, pressure head gradients in the soil are created by the root uptake processes of the plants which result in transpiration from the plant. Therefore, ψ_s will be affected by the root-water pressure head which in turn depends on R_d (Tracy et al, 1994, Muralidharan, 1994). Consequently, modeling phytoremediation involves a root-water pressure head coupled with a soil-water pressure head

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in order to represent the macroscopic root-soil water flow in the rhizosphere environment (Tracy et al, 1993, Tracy et al, 1994). The following equations are called the root-soil water flow model. In the soil,

$$\frac{\partial}{\partial x}\left[K_{sx}\frac{\partial}{\partial x}(\psi_s)\right] + \frac{\partial}{\partial z}\left[K_{sz}\frac{\partial}{\partial z}(\psi_s+z)\right] - q = \left[\beta S_s + S_y\frac{dS_e}{d\psi_s}\right]\frac{\partial \psi_s}{\partial t} \qquad (13)$$

In the roots,

$$\frac{\partial}{\partial x}\left[K_{rx}\frac{\partial}{\partial x}(\psi_r)\right] + \frac{\partial}{\partial z}\left[K_{rz}\frac{\partial}{\partial z}(\psi_r+z)\right] + q = R_d\frac{\partial}{\partial t}WC_r + WC_r\frac{\partial R_d}{\partial t} \qquad (14)$$

The rate of soil-water uptake (q) by the plants' root system is expressed as

$$q = S_e R_d \Gamma(\psi_s - \psi_r) \qquad (15)$$

where Γ is a parameter describing permeability of the plants' root system.

7.4. Model verification

The contaminant fate model coupled with the root-soil water flow model was employed to simulate a laboratory chamber with alfalfa plants growing under laboratory conditions. Plants were fed daily from the bottom of the chamber for nearly a year with ground water contaminated with toluene at a concentration of 500 mg/L. Tracer studies were initially performed to study dispersion characteristics of the soil and comparison with tracer simulation results was accomplished (Muralidharan et al, 1995b, Muralidharan, 1994). Initial and boundary conditions for modeling the plant growing chamber contaminated with toluene were developed based on the physical setup of the laboratory chamber (Muralidharan, 1994).

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Experimental observations of the plant growth chamber indicated that toluene concentration remained relatively constant in the saturated zone of the chamber (Davis et al, 1994). Headspace measurements above the plants in the chamber were accomplished using FT-IR instrumentation to detect either volatilization of toluene through the soil gas pathway or transpiration through the plant pathway (Davis et al, 1994). Observations indicated that toluene concentration was consistently below limits of detection of the instrument which was less than 1 ppm (Davis et al, 1994).

Modeling results indicate that toluene was attenuated in the plant growth chamber. Simulations also revealed that toluene concentrations remained relatively constant in the saturated zone of the soil and decreased from the saturated zone to the soil surface where the concentration was close to 0 ppm (Muralidharan et al, 1995b). Table 3 shows a comparison of experimental and simulated values of toluene at different sampling points in the saturated zone.

Basically, modeling data supported the concept that the rhizosphere of alfalfa plants which sustains a genetically diverse microbial consortium of aerobic microorganisms was responsible for the predominant loss of toluene in the plant chamber. Table 4 shows a comparison of the degree of soil-water saturation collected after one year of operation of the system.

The model was also used to make comparison of the washout patterns of toluene from the plant chamber. Good consistency between simulated and experimental concentrations was observed. Overall, the model was able to predict fate of the contaminants during phytoremediation (Tracy et al, 1994, Muralidharan, 1994).

8. Modeling plant based remediation -- other applications

Santharam et al (1994) modeled the process of degradation of polycyclic aromatic hydrocarbons (PAH) using as an experimental base the studies of Reilley (1993) (Schwab and Banks 1994, Erickson et al 1994b). The contaminant is assumed to be dispersed in small blobs of pure material with a low concentration in the surrounding aqueous phase accessible for microbial use. Mass balance equations are derived from Davis et al (1993). Key conclusions from these simulations are (1) that a heterogenous size distribution of the initial PAH blobs is necessary to describe the rate of disappearance; (2) that plants or their organic acid exudates, by enhancing the microbial population density, hasten the rate of remediation; and (3) that for low solubility compounds, very little is taken up into the plants compared to the amount degraded by microbes.

Modeling of water abstraction and remediation has been done for several contaminants using data from a landfill soil near Manhattan, KS (Davis et al, 1993). The particular instance cited is for atrazine remediation, with poplars as the plant. The initial water table is assumed to be at 1.5 m and tree root density decreases almost linearly from surface to water table. No removal other than plant uptake is assumed in this simple model. During the summer months when there is considerably more evaporation than precipitation, the amount of contaminant passing under a vegetated area in ground water decreases markedly. In the winter, when vegetation is dormant and there is a net gain of surface water, the amount of contaminant leaving the planted area (a 5 m wide belt) rebounds. For a five year contaminant input and total eight year simulation, net ground water efflux of contaminant from a vegetated area is estimated to be 40% lower for a vegetated than an unvegetated area. In the model, contaminant is primarily

withdrawn from the upper portion of the water table and there is little mixing between layers. Consequently, a plant-based remediation can be successful only to the extent that plants can withdraw sufficient water to lower the water table making for a deeper aerobic vadose zone, or if the contaminant is a light non-aqueous phase liquid that does not tend to sink to the bottom of the permeable zone.

A recent study by Tracy et al (1994) used an improved version of the above model, BIOROOT, to examine total precipitation, evapotranspiration, and their interaction on a non-volatile compound with all other properties being those of benzene. Microbial degradation is permitted in this model, with rates adjustable to reflect realistic estimates of microbial activity and biomass. Transport and degradation under a planting of alfalfa were examined over the course of the growing season (20 weeks) in 11 different years. Precipitation and Pet data from a station near Manhattan, KS, were used. The contaminant was assumed to be initially distributed uniformly throughout the upper 3 m of sandy soil and root distribution was assumed to be that of alfalfa under irrigation because data is available (Stanberry, 1955). Precipitation varied from <0.2 to >1.0 m / yr, with a precipitation deficit in all but the wettest year. The greater the precipitation deficit, the less benzene leached below 4 m. In 8 of 11 years only 3% of the contaminant passed below 4 m within 20 weeks during the growing season. Of course during the dormant season some leaching will occur, although in this climate the large majority of the rain falls within the growing season.

One limitation of the model is that it does not account for additional nutrient requirements that may arise (Stotzky and Norman, 1961) when high amounts of carbon substrate allow production of a high microbial biomass which in turn drives the oxygen or other limiting nutrient

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level very low. Nevertheless, the model accurately accounts for the observed degradation of toluene as it passes along a 1.8 m long channel as discussed in the Model verification section.

9. Plant genetic engineering

A recent article by Stomp et al (1994) considers some strategies for engineering plants to improve bioremediation. One of the simpler approaches is to make use of the organism *Agrobacterium rhizogenes* to induce a state called hairy root disease. Depending on virulence of the strain used, extent of root production is variable, but generally infection leads to a significant enhancement of rooting without obvious detrimental effects on the host plant. Increased root mass has the apparent advantage of increasing the surface area available for microbial colonization. Root exudation may be increased in proportion to increase in root area. Such rhizosphere enhancements could improve bioremediation potential of the plant-microbial system. It is suggested that when water is not freely available in unlimited quantities, increased root mass could lead to greater water uptake, and hence greater contaminant mobilization and potential degradation.

Genetic engineering of plants by insertion of genes for chlorinated phenolics catabolism is in progress (Stomp et al, 1994). These enzymes may allow metabolism of TCE. Toluene dioxygenase, which is phenol-inducible, is effective (Nelson et al, 1988). Stomp et al (1994) also cite unpublished work of Wilbert and Gordon showing highly effective uptake of ^{14}C-labeled TCE by poplars and its conversion to non-extractable forms, nonvolatile polar catabolites. A number of companies have introduced genes for degradation of herbicides into crop plants. Some of these approaches could prove useful for remediation of other contaminants.

10. Design considerations

There is still too little known about the capabilities of plants to identify optimum species. In most cases rapidly growing, indeterminate species are preferred for their ability to use water as discussed above. However, for long term closure of landfills in temperate climates, it might be desirable to use higher value hardwood trees such as walnut or pecan, in addition to fast-growing poplars, unless there is a ready market for poplar products. Walnuts or pecans under good fertility conditions use large amounts of water and produce both nuts and wood. In sub-tropical regions, eucalyptus would be more appropriate than poplars. Water use features of eucalypts vary widely between species (Calder, 1992). Likewise, one would use alfalfa only in a situation where a short-lived perennial is satisfactory. Replanting would be necessary after a few years, if the remediation were not completed in that time. It is essential to choose climatically adapted species from among those with desired growth characteristics.

Pump-and-treat processes are often designed to contain contaminants and prevent plume migration. Vegetation can be designed to pump-and-treat contaminated ground water, based on the estimated amount of water that selected plants evapotranspire, and the historic precipitation record. Simulations of the proposed design can be carried out based on past precipitation records, measured contaminant concentrations, and hydrogeological precipitation records (Tracy et al, 1994).

Table 5 reports mass balance data for toluene, phenol, 1,1,1-trichloroethane, and trichloroethylene in the laboratory chamber with alfalfa plants which has been described previously (Davis et al, 1994, Muralidharan et al, 1995a,b). The mass of contaminant leaving in the ground water depends in part on the fraction of water which leaves the chamber as ground

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water. For a given field site, vegetation sufficient to evapotranspire all of the contaminated water may be preferable. Losses of contaminants in the gas phase depend on volatility and biodegradability of the contaminants, depth to ground water, as well as the mix of plants selected for phytoremediation. Further research is needed to predict losses to the gas phase for contaminants.

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Acknowledgments

Table 1. Beneficial effects of plants in contaminated soil.

Plants supply nutrients which sustain microbial populations in the rhizosphere.

Plants utilize solar energy to pump contaminated water into the vadose zone and rhizosphere.

Plants lower the water table so that oxygen transfer by gas phase diffusion is enhanced.

Plants add organic matter to soil which provides sites for adsorption and binding of contaminants.

Plants pump-and-treat contaminated water using solar energy and natural processes.

Plants reduce contaminant transport in wind blown dust and sediment.

Plants can contain and treat contaminants efficiently and inexpensively.

Table 2. Bioenergetics of root exudation and microbial processes in the rhizosphere.[*]

Process	Amount
Solar energy supplied	15,000 kJ $m^{-2}d^{-1}$
Solar energy incorporated into chemical energy	0.7 - 3% 250 kJ $m^{-2}d^{-1}$
Chemical energy transported to the root zone	30 - 50% 100 kJ $m^{-2}d^{-1}$
Chemical energy in root exudates	45 kJ $m^{-2}d^{-1}$
Carbon dioxide production from oxidation of root exudates	100 mmoles $m^{-2}d^{-1}$

[*] From Erickson et al (1994a, 1995)

Table 3: Experimental and simulated values of toluene in the saturated zone of the plant chamber.

Sampling Wells (distance from inlet in cm)	Experimental Values[*] (mg/L)	Simulated Values (mg/L)
Port 1 (33)	434	389
Port 2 (66)	418	446
Port 3 (114)	421	461
Port 4 (147)	403	457
Outlet (180)	455	368

[*] Mean concentration (n > 10) (Muralidharan et al, 1995b, Muralidharan, 1994).

Table 4: Comparison of experimental and simulated values of degree of soil-water saturation

in the channel soil after one year of operation.

Soil Depth (cm)	Distance along the axial length of the channel (cm)					
	20		80		160	
	Expt.*	Sim.**	Expt.	Sim.	Expt.	Sim.
10	0.79	0.72	0.77	0.71	0.76	0.70
20	0.95	0.87	0.91	0.86	0.90	0.85
30	0.99	1.00	0.98	1.00	0.95	1.00

*   Expt. = Experimental Value
**   Sim.   = Simulated Value

Table 5. Mass balances for toluene, phenol, 1,1,1-trichloroethane and trichloroethylene in a laboratory chamber with alfalfa plants.

Compound	Fraction in exiting groundwater	Fraction in gas phase outflow	Fraction disappearing in the chamber
Toluene	0.39	0	0.61
Phenol	0.01	0	0.99
1,1,1-trichloroethane	0.21	0.21	0.58
trichloroethylene	0.20	0.16	0.64

* Based on results presented in Erickson et al (1994b) and Muralidharan et al (1995a,b).

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1

Mining and its Environmental Impact

ROYAL
SOCIETY OF
CHEMISTRY

Vegetative Remediation at Superfund Sites

G. M. PIERZYNSKI, J. L. SCHNOOR, M. K. BANKS,
J. C. TRACY, L. A. LICHT, AND L. E. ERICKSON

1 Introduction

Non-ferrous metal mining activities across the world have produced a variety of environmental problems. Three types of contamination created by large-scale metal extraction have been identified.[1] Waste-rock, tailings, and slag are primary contaminants. Secondary contamination occurs in groundwater beneath open pits and ponds, sediments in river channels and reservoirs, floodplain soils impacted by contaminated sediment, and soil affected by smelter emissions. River sediments reworked from floodplains and groundwater from contaminated reservoir sediments were identified as tertiary contaminants. In the United States, many of these contaminated sites have been classified as Superfund sites, which dictates that some remedial action be taken in the future.

The metals or metalloids most commonly found at Superfund sites are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), and zinc (Zn).[2] Most of the discussion will focus on As, Cd, Pb, and Zn as elements of concern for two Superfund sites: the Whitewood Creek in the Black Hills of western South Dakota and the Galena site located in southeastern Kansas. Contamination of surface water and groundwater with As and Cd from over one hundred years of gold mining activity is the principal concern at the Whitewood Creek site. The Galena site is located in the Tri-State mining region (southeast Kansas, southwest Missouri, and northeast Oklahoma), where Pb and Zn sulfide ores were mined and smelted extensively from the mid-1800s to approximately the 1950s. Pb and Zn contaminated mine spoils, soils, groundwater, and surface water are extensive problems in the Tri-State Region.

There are two primary reasons for concern over elevated concentrations of trace elements in waters, soils, or mine spoils. First, elevated human and animal exposure to the metals can occur through food chain transfer, ingestion of wind-blown dusts, or direct ingestion of soil. Persons living downwind of an old smelter site in the Tri-State region could consume at least 50% more Pb and Cd by eating some of their home-produced food items than by eating comparable

[1] J. N. Moore and S. N. Luoma, *Environ. Sci. Technol.*, 1990, **24**, 1278–1285.
[2] J. E. McLean and B. E. Bledsoe, 'Behavior of Metals in Soils', EPA Ground Water Issue, EPA/540/S-92/018, US Environmental Protection Agency, Washington, DC, 1992.

Table 1 Remediation options for metal-contaminated sites

Method	Comments
Excavation followed by:	
Solidification	Addition of cementing agent to produce a hardened, non-porous, non-leachable material.
Vitrification	Heating to produce a glass-like, non-porous, non-leachable material.
Washing	Chelate or acid extraction.
Leaching	Pile or batch leaching with chelates or acids.
Particle size segregation	Selective removal of finer particle sizes (*e.g.* clay) that have the highest metal concentrations.
In situ	
Solidification	As described above.
Vitrification	As described above.
Encapsulation	Cover site with impermeable layer.
Attenuation	Dilution with uncontaminated material.
Volatilization	Promote formation of volatile methylated species (Se, As, Hg).
Vegetative	Promote vegetative growth by providing proper fertility and water availability, reducing metal bioavailability, and/or using metal-tolerant plant species.

items purchased in a control area.[3] Epidemiological studies have shown a significantly higher prevalence of chronic kidney disease, heart disease, skin cancer, and anemia in persons living for more than 5 years in Galena, KS, than in the populations of two nearby control towns.[4] Inhalation of As has been associated with lung cancer, and ingestion of As is judged to cause skin cancer.[5] The second reason for concern relates to the phytotoxic potential of the metals, which can limit biomass production.[6,7] This inhibition of plant growth can have direct negative effects, such as a limitation of crop yields. The effects also can be indirect. For example, the lack of vegetative cover probably will result in enhanced wind and water erosion, which further disperses the contaminants and increases the likelihood of human exposure via wind-blown dusts.

Numerous remediation options exist for metal-contaminated sites, as shown in Table 1. An excellent description of some experimental methods has been published.[8] The methods requiring excavation have a significant drawback given that the volume of material to be treated can be quite large. For example,

3 J. V. Lagerwerff and D. L. Brower, in 'Trace Substances in Environmental Health, Vol. 8, ed. D. D. Hemphill, University of Missouri, Columbia, MO, 1974.

4 J. S. Neuberger, M. Mulhall, M. C. Pomatto, J. Sheverbush, and R. S. Hassanein, *Sci. Total Environ.*, 1990, **94**, 261–272.

5 D. W. North, *Environ. Geochem. Health*, 1992, **14**, 59–62.

6 S. B. Bradley and J. J. Cox, *Sci. Total Environ.*, 1986, **50**, 103–128.

7 G. M. Pierzynski and A. P. Schwab, *J. Environ. Qual.*, 1993, **22**, 247–254.

8 United States Environmental Protection Agency, 'The Superfund Innovative Technology Evaluation Program: Technology Profiles', (ed. 5) EPA/S40/R-92/077. US Government Printing Office, Washington, DC, 1992.

Cherokee County, KS (which contains the Galena Superfund site) has numerous abandoned Pb and Zn mining and smelter sites. The soil survey for the county reports 1316 hectares of mine dump sites,[9] which have high Pb and Zn concentrations and would benefit from remediation. If only the top 300 mm of these areas were treated, this would involve approximately 4.8×10^6 Mg of material (1 Mg $\equiv$ 1 tonne). This is a conservative estimate, because most areas would require more than the top 300 mm be treated, and some areas that need remediation are not shown in the soil survey.

The beneficial effects of plants in remediation of soil and groundwater contaminated with hazardous organic compounds have been presented.[10] The vegetative remediation methods for metal contaminated sites, which are the focus of this paper, can utilize amendments that reduce metal bioavailability as well as metal-tolerant plant species with the goal of establishing a vegetative cover sufficiently dense to prevent wind and water erosion and that will remain viable for extended periods. The vegetation can be native or introduced grasses, forbs, or trees. The advantages of vegetative remediation include the minimization of wind and water erosion, lower cost as compared with other remediation options, improvement of aesthetics, no production of waste products, increases in soil organic C concentrations (binds metals, improves soil tilth, *etc.*), and the potential to serve as a temporary remediation until more suitable methods are funded or developed. In addition, modeling efforts suggest that vegetation, particularly trees, probably would reduce net percolation through the soil or mine spoil material and reduce the leaching potential of the metals. Disadvantages include the lack of data on the long-term viability of the vegetation, the possibility of producing metal-rich plants that could be consumed by wildlife or other animals, the lack of transpiration by the plants during certain periods of the year, and the possibility of transport of radionuclides or metals in mixed wastes due to excretion of soluble exudates by plant roots.

The goals of this article are to briefly describe the chemical and microbiological environment in mine spoils and contaminated soils, to describe several case studies where vegetation has been used in remediation of Superfund mine sites, and to present a generalized model that can aid in predicting the effects of vegetation on a contaminated site.

2 Chemical Aspects of Metal-contaminated Soils and Mine Spoils

Chemical characteristics such as total metal concentrations, pH, cation exchange capacity, plant nutrient concentrations, and organic C content in contaminated soils and mine spoils can vary considerably. English soils having less than 50% vegetative cover contained 1660 mg kg^{-1} Pb and 4230 mg kg^{-1} Zn in the surface 50 mm.[11] Soils with vegetation exhibiting heavy metal chlorosis had 323 mg kg^{-1} Pb and 676 mg kg^{-1} Zn in the top 50 mm.[6] Zn and Pb concentrations as high as

[9] Soil Survey Staff, 'Soil Survey of Cherokee County, Kansas', USDA Soil Conservation Service, US Government Printing Office, Washington, DC, 1985.

[10] J. F. Shimp, J. C. Tracy, L. C. Davis, E. Lee, W. Huang, and L. E. Erickson, *Crit. Rev. Environ. Sci. Technol.*, 1993, **23**, 41–77.

[11] M. S. Johnson and J. W. Eaton, *J. Environ. Qual.*, 1980, **9**, 175–179.

43 750 and 4500 mg kg^{-1}, respectively, have been reported for mine spoil material.[12] Gold mine tailing in South Dakota contained 917 mg kg^{-1} As.[13] In the United States, the Toxicity Characteristic Leaching Potential (TCLP) is used to classify materials as hazardous or not.[14] The procedure involves a single extraction with 0.1 M acetic acid in an effort to simulate leaching conditions that a waste might experience. If the concentrations of certain metals exceed some standard values, the material is classified as hazardous.

The pH of the contaminated soils or mine spoil materials can range from values as low as 2.0 to as high as 8.0. The very acid conditions typically are associated with the weathering of sulfide-bearing minerals. The alkaline conditions can be caused by the presence of a calcareous matrix. In terms of cation exchange capacities, plant nutrient concentrations, and organic C concentrations, one can consider contaminated soils and mine spoils as diluted soils. That is, these parameters will range from extremely low values (highly diluted) to those typical for soils (not diluted). Indeed, low fertility because of low cation exchange capacities and plant nutrient concentrations and low water holding capacities because of low organic C concentrations are as limiting as metal phytotoxicities in establishment of vegetation in mine spoil materials.

The behavior of metals in soils has been reviewed.[2] Most metals interact with the inorganic and organic matter that is present in the root–soil environment; potential pools or forms of metals include those dissolved in the soil solution, adsorbed to the vegetation's root system, adsorbed to insoluble organic matter, bonded to exchange sites on inorganic soil constituents, precipitated or coprecipitated as solids, and within the soil biomass. Generally, the total metal concentration in soil is a poor indicator of metal availability to plants. The concept of metal bioavailability, in the context of soils and mine spoils, refers to some sub-fraction of the total amount of a metal that best correlates to plant response. That response is typically measured in terms of biomass production or metal concentrations in plant tissue. Any of the pools or forms of metals described above can contribute to the bioavailable fraction. In practice, metal bioavailability is often operationally defined as that extracted with a particular extractant.

Metals present in the soil solution can be free metal ions, soluble complexes with organic or inorganic ligands, or associated with mobile colloidal materials. Soil solution studies generally show that plant response to metals is correlated with the free metal ion activity. Therefore, one aspect of metal bioavailability is related to which factor or factors contribute to the activity of the free metal ion in the soil solution. These interactions are summarized in Figure 1. Equilibrium models often are used to estimate free metal ion activities. The difficulty with the application of these models in the soil–root environment is associated with properly modeling all of the interactions identified above.

[12] G. M. Pierzynski and A. P. Schwab, in Proceedings of the Conference on Hazardous Waste Research, ed. L. E. Erickson, Manhattan, KS, 1990, pp. 511–520.

[13] D. F. Aoki, 'The Uptake of Arsenic and Cadmium in Mine Tailings by Poplar Trees', MS Thesis, University of Iowa, Iowa City, IA, 1992.

[14] US Environmental Protection Agency, 'Test Methods for Evaluating Solid Waste: Physical/Chemical Methods', SW-846. USEPA, Office of Solid Waste and Emergency Response, Washington, DC, 1986.

Figure 1 Processes influencing free metal ion activities in soil solutions
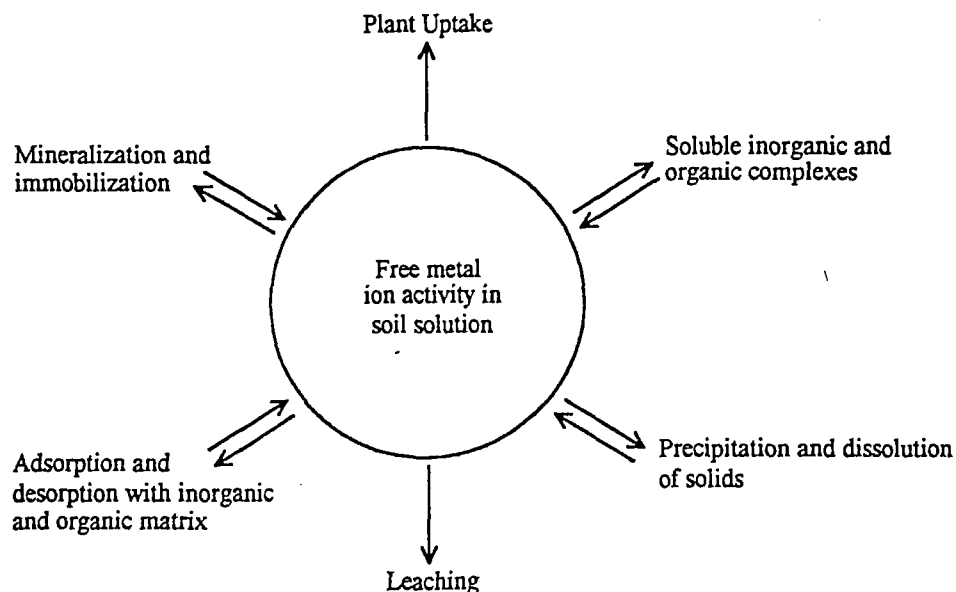
Metal fractionation or sequential extraction schemes sometimes are used to describe metal behavior in soils.[7] The schemes cannot be entirely specific for a given fraction within the soil, and an additional problem of re-adsorption of extracted metals to the soil constituents exists. Therefore, the value of the schemes in obtaining information on fundamental processes that influence metal behavior in soils is limited. However, the schemes can be useful in an empirical sense.

Remediation of a metal-contaminated site can include three possible changes in the chemical characteristics of the soil or mine spoil material. The total metal concentration can be reduced, as is the case with washing or leaching procedures. The TCLP concentration can be reduced without removing any of the metal, as is the case with solidification or vitrification processes. The metal bioavailability can also be reduced. *In situ* methods for reducing bioavailability include sorption, ion exchange, precipitation, and attenuation.[15] Increasing soil pH also has been evaluated for cationic metals.[7] Little information has been published with regard to the effectiveness of the soil treatments other than data on yield and metal concentrations in plant tissue.[16,17] In particular, detailed studies of the effects of soil amendments on free metal ion activities have not been reported. This is partly due to a lack of the necessary thermodynamic data.

3 Microbial Aspects of Metal-contaminated Soils and Mine Spoils

Plants may accumulate as much as 10 000 mg of Zn or 2500 mg of Pb per gram of shoot biomass.[18] Heavy metal tolerant plant species which concentrate and

[15] R. Sims, D. Sorensen, J. Sims, J. McLean, R. Mahmood, R. Dupont, J. Jurinak, and K. Wagner, 'Contaminated Surface Soils In-place Treatment Techniques', Noyes Publications, Park Ridge, NJ, 1986.
[16] M. S. Johnson, T. McNeilly, and P. D. Putwain, *Environ. Pollut.*, 1977, **12**, 261–277.
[17] W. E. Sopper, *Landscape Urban Planning*, 1989, **17**, 241–250.
[18] A. J. M. Baker, *J. Plant Nutr.*, 1981, **3**, 643–654.

detoxify metals in above ground plant parts are known as accumulator species. Detoxification mechanisms for these species may include binding of heavy metals to cell walls, pumping heavy metal ions into vacuoles, or complexing of heavy metals by organic acids. In contrast, excluder plants species may absorb heavy metals but restrict their transport into shoots. This type of heavy metal tolerance does not prevent uptake of heavy metals but restricts translocation, and detoxification of the metals takes place in the roots. Mechanisms proposed for excluder detoxification include immobilization of heavy metals on cell walls, exudation of chelate ligands, or formation of a redox or pH barrier at the plasma membrane.[19] Microbial immobilization of heavy metals in the root zone would also reduce availability to and uptake by plants.

In contaminated sites, heavy metal concentrations may be high enough to inhibit microbial activity. Soil micro-organisms may be critical to plant growth because they encourage development of a stable soil structure, release required nutrients in inorganic forms by mineralization, and produce growth-regulating substances. Also, soil micro-organisms may contribute to plant growth by immobilizing heavy metals in soil. The direct effects of Cd, Cu, Zn, and Pb on soil micro-organisms are generally understood.[20] Heavy metal contamination of soil decreases microbial activity, microbial numbers, and microbially mediated soil processes such as nitrification, denitrification, and decomposition of organic matter.[21-24] Higher numbers of resistance bacteria are found in heavy metal contaminated soil than in uncontaminated soil, and resistant communities isolated from long-term contaminated soils are more diverse than those found in recently contaminated soils.[25-28] However, at extremely high levels of contamination, fewer resistant bacteria have been isolated than from less polluted soils.[24]

Previous research has indicated that microbes can bind metals. Micro-organisms may accumulate metal ions by complexation with extracellular polymers,[29] or by ion exchange with polyanions of the bacterial cell wall.[30] Gram-positive bacteria have a greater ability to bind metals than Gram-negative bacteria due to cell wall structural differences,[31] although it has been suggested that the Gram-negative cell envelope acts to impede metal ion entry into the cell interior. Bacteria may be able to transform heavy metals by the production of

[19] G. T. Taylor, *J. Plant Nutr.*, 1987, **10**, 1213–1222.
[20] E. Baath, *Water Air Soil Pollut.*, 1989, **47**, 335–379.
[21] F. H. Chang and F. E. Broadbent, *Soil Sci.*, 1981, **132**, 416–421.
[22] A. Nordgren, E. Baath, and B. Soederstroem, *Soil Biol. Biochem.*, 1988, **20**, 949–954.
[23] J. M. Bollag and W. Barabasz, *J. Environ. Qual.*, 1984, **11**, 196–201.
[24] P. Doelman and L. Haanstra, *Soil Biol. Biochem.*, 1979, **11**, 487–491.
[25] B. H. Olsen and I. Thornton, *J. Soil Sci.*, 1982, **33**, 271–277.
[26] M. Kiroki, *Soil Sci. Plant Nutr.*, 1992, **38**, 141–147.
[27] K. G. Shetty, M. K. Banks, B. A. Hetrick, and A. P. Schwab, *Water Air Soil Pollut.*, 1993, accepted.
[28] T. J. Beveridge, in 'Metal Ions and Bacteria', ed. T. J. Beveridge and R. J. Doyle, John Wiley and Sons, Inc., New York, NY, 1989, 1–29.
[29] G. Bitton and V. Freihofer, *Microb. Ecol.*, 1978, **4**, 119–125.
[30] T. Rudd, R. M. Sterritt, and J. N. Lester, *Microb. Ecol.*, 1983, **9**, 261–272.
[31] T. J. Beveridge and S. F. Koval, *Appl. Environ. Microb.*, 1981, **42**, 315–335.

water-soluble organics which would increase metal solubility,[32] or release metals previously bound due to variations in metabolism or growth.[33]

The soil fungal population may similarly be affected by heavy metal contamination, with the diversity of micro- and macro-fungi decreasing in contaminated soils.[34] In the higher fungi, the production of sporophores is a sensitive measure of metal pollution.[20] One specific group of fungi, the mycorrhizal fungi, can directly contribute to plant tolerance of heavy metals. Mycorrhizal fungi are plant symbionts which proliferate inside and outside of host plant roots. The hyphal strands of the fungus exterior to the root absorb nutrients and translocate them into the plant. These fungi can bind metals to hyphae, restricting them from translocation to shoots.[35] To what extent mycorrhizal symbiosis affects heavy metal translocation patterns expressed by plants is not known.

The effect of vegetation on groundwater contamination by leachate from contaminated soils is uncertain.[36] The mobilization of biologically available metals may be slightly higher in vegetated soil[37] due to the release of complexing agents by the plant. The concentration of Zn in the leachate from contaminated mine tailings is higher in soils treated with 1.0 mM succinic acid than in the absence of organic acid (Table 2).[38] The adsorption of heavy metals to soil may also decrease in the presence of organic ligands found in the rhizosphere.[39] Plant roots may also influence water transport and metal movement by providing flow channels in the soil. Other research indicates that heavy metal leachate may be affected by the type of soil microflora associated with the plant (Table 3). Revegetation of heavy metal contaminated soil may increase heavy metal leaching, especially if soil microflora have not been fully restored.[40]

4 Vegetative Remediation at Mine Sites: Case Studies

Whitewood Creek

Revegetating mine sites and metal wastes offers several advantages that have been under-appreciated in the literature. Fast growing hybrid poplar trees have been used in a variety of climate zones in riparian area applications to stabilize soils, decrease wind-blown dust, and decrease vertical migration of pollutants. Most risk assessments at mine tailings sites indicate that the largest cancer risk for elements like As and the largest chronic health risk to humans from elements such as Cd are due to inhalation of wind-blown dust or ingestion of aeolian-deposited soil by children. Vegetation can decrease these exposure pathways

[32] A.J. Francis, S. Dobbs, and B.J. Nine, *Appl. Environ. Microb.*, 1980, **40**, 108–113.

[33] C.A. Flemming, F.G. Ferris, T.J. Beveridge, and G.W. Bailey, *Appl. Environ. Microb.*, 1990, **56**, 3191–4203.

[34] H. Yamamoto, K. Tatsuyana, and T. Uchiwa, *Soil Biol. Biochem.*, 1985, **17**, 785–790.

[35] R. Bradley, A.J. Burt, and D.J. Read, *New Phytol.*, 1981, **91**, 197–209.

[36] F.L. Domergue and J.C. Vedy, *Int. J. Environ. Anal. Chem.*, 1992, **46**, 13–23.

[37] J.M. Besser and C.F. Rabeni, *Environ. Toxicol. Chem.*, 1987, **6**, 879–890.

[38] M.K. Banks, C.Y. Waters, and A.P. Schwab, *J. Environ. Sci. Health*, 1993, accepted.

[39] P. Chairidchai and G.S.P. Ritchie, *Soil Sci. Soc. Am. J.*, 1990, **54**, 1242–1248.

[40] M.K. Banks, G.R. Fleming, A.P. Schwab, and B.A. Hetrick, *Chemosphere*, 1993, accepted.

Table 2 Average zinc concentration in the leachate of organic acid amended mine tailings[38]

| | *Average Zinc Concentration in Leachate*/$\mu g\, l^{-1}$ | | | |
| | *Acid Concentration*/μm | | | |
Type of Acid	0	50	250	1000
Formic	361	423	352	332
Succinic	362	308	492	506

Table 3 Average concentration of zinc leached from heavy metal contaminated soil by varying plant and microbial treatment[40]

Treatment	*Zinc*/mg l^{-1}
With plants	
Unamended	371
Microbes	228
Mycorrhizae	360
Microbes and Mycorrhizae	271
No plants	
Unamended	263
Microbes and Mycorrhizae	189

dramatically. Revegetation can be considered as a remediation method or used in tandem with other techniques for stabilizing soils and closing sites at low cost.

If contamination is in the upper 2–3 m of soil, deep-rooted poplar trees can significantly decrease the downward migration of leachate via evapotranspiration.[41] The trees start from 2 m 'whips', cuttings that have preformed root initials. When planted at a depth of 2 m, they form a dense root mass that will take up large quantities of moisture, increase soil suction, and decrease downward migration of pollutants. In the dormant season, some leakage of water can occur through the system but, precipitation is not great during this period. The trees grow 2 m in the first growing season and reach a height of 6–8 m after three years when planted at a density of 10 000 trees per hectare. Carbon fixation is approximately 2.5 kg m^{-2} yr^{-1}. Various management schemes can be adopted, and the trees can remain with very little attention for twenty years or more after the second season.

Advantages and disadvantages of vegetative remediation were discussed previously. Additional concerns specifically for trees include leaf litter and whether associated toxic residues might be blown off site. This concern may be tested in the laboratory or field to determine whether uptake and translocation of the metals into the leaves of trees or grasses exceed standards. In general, Cd and As (arsenate) are the most problematic because of their chemical similarity to nutrients (Ca, Zn, and P). Pb, Cr, Hg, and other metals are of lesser concern because of smaller rates of uptake. Following is a case study that illustrates an investigation of this potential problem at a Superfund site.

[41] L. Licht, 'Poplar Tree Buffer Strips Grown in Riparian Zones for Biomass Production and Non-point Source Pollution Control', PhD Dissertation, Civil and Environmental Engineering, The University of Iowa, Iowa City, IA, August, 1990.

Figure 2 Cumulative growth curves for poplar trees in three fertilized laboratory treatments of 0, 50, or 100% mine tailings[13]
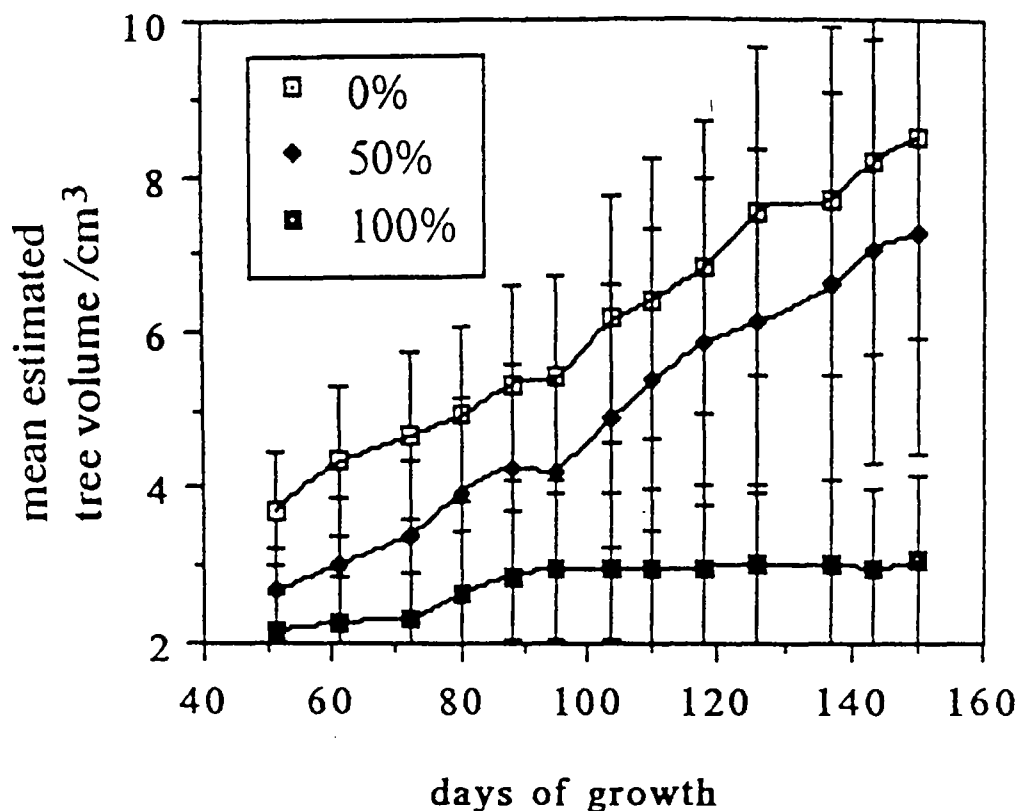
An eighteen mile stretch of Whitewood Creek is a US Superfund site because of contamination of surface water and groundwater with As and Cd (arsenopyrite is the major mineral in the tailings) from 130 years of gold mining activity. It is located in the Black Hills of extreme western South Dakota below the town of Whitewood. Chemical characterization indicated that the tailings contained an average of 1250 mg kg^{-1} total As and 9.4 mg kg^{-1} total Cd with pH ranging from 3.9 to 5.4. Plant-available P and K levels were quite low. An experimental plot was planted with 3100 hybrid poplar trees to a depth of 1.6 m in April of 1991. A commercial NPK fertilizer was used at recommended rates to ensure vigorous early growth of the cuttings. Roots formed along the entire length of the cutting in the soil, so a dense root mass was established that takes up infiltration and intercepts interflow moving towards the creek.

Genetically identical cuttings also were established in a plant incubator in the laboratory.[13] Figure 2 shows that the cuttings established in 100% mine tailings, the worst case from the site, grew more slowly than the other trees under optimal conditions in the laboratory. All trees were fed Hoagland R growth medium containing major nutrients. Other treatments were grown in a mixture of mine tailings and peat: vermiculite (50:50 by mass mixture). The treatment with 0% mine tailings was composed of a peat: vermiculite mixture, ideal for plant growth.

At the end of the first growing season, the trees had grown to 12 m at the field site. Leaves, stems, and roots were collected from the field as well as the laboratory trees to compare As and Cd uptake and translocation. Poplar leaves in the field did not accumulate significant amounts of As or Cd (Figures 3 and 4). These concentrations are below most levels established for field application of municipal sewage sludge or compost. Furthermore, they are well below the

Figure 3 Total acid-digestable As in leaves, stems, and roots in fertilized laboratory (0, 50, or 100% mine tailings) and field poplars[13]
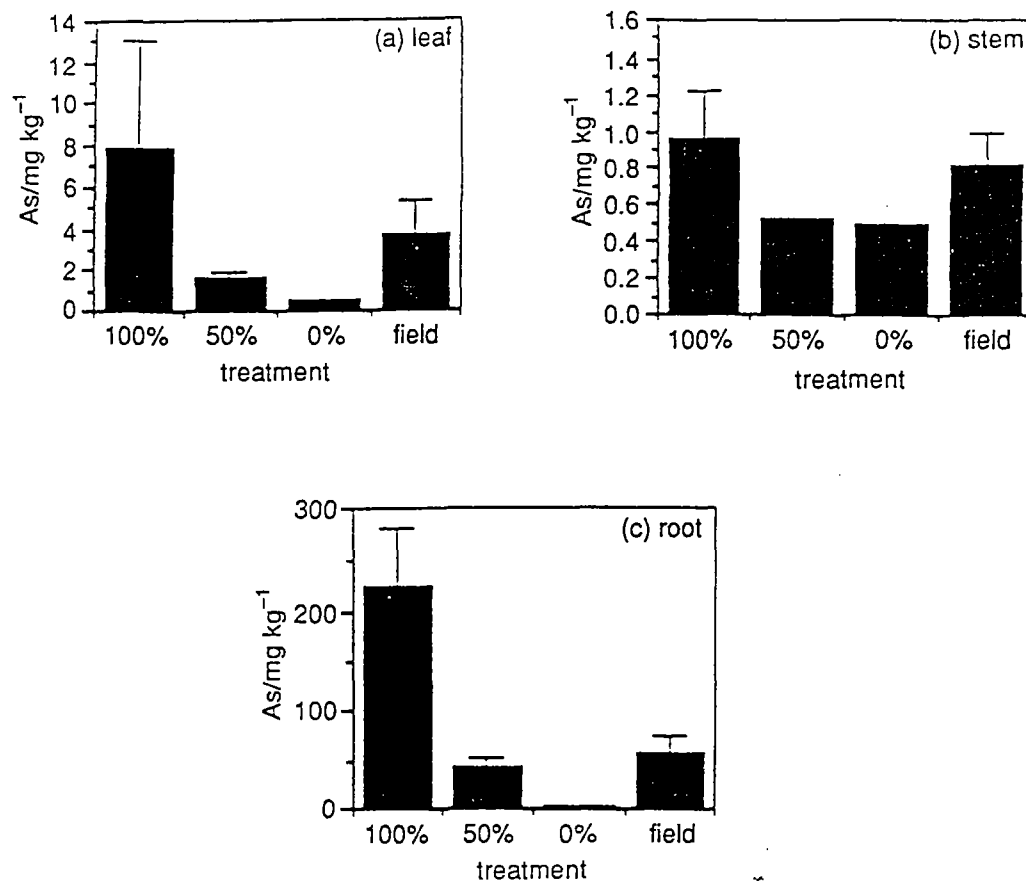
Figure 4 Total acid-digestable Cd in leaves, stems, and roots in fertilized laboratory (0, 50, or 100% mine tailings) and field poplars[13]
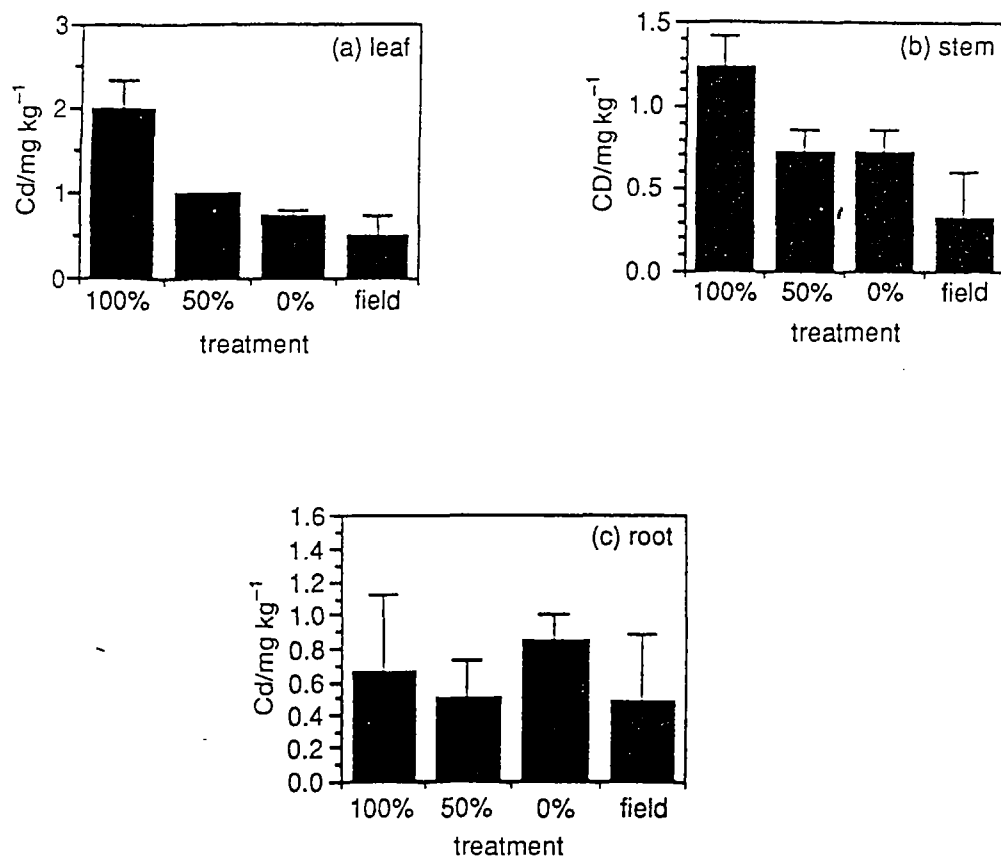
reference concentrations accumulated by leaves in the laboratory treatments of 100% mine tailings, indicating that the laboratory study overestimated the amount that would be accumulated in the field, possibly because of ideal growth conditions in the laboratory. It is interesting to note that the commercial peat : vermiculite mixture allowed a greater uptake of Cd by leaves than did the field situation (Figure 4a). Small amounts of Cd are always present in most commercial nursery mulches and soil amendments.

Concentrations of Cd and As in native vegetation at the site were generally of the same order of magnitude as those in poplar trees. But the leaves of lambsquarter were particularly high in As ($14\,mg\,kg^{-1}$), and the leaves of the native cottonwoods (a cousin of the hybrid poplar trees) have a somewhat higher concentration ($1.6\,mg\,kg^{-1}$) than leaves of the poplars planted for vegetative remediation. Results indicate that the poplars are not a serious concern in terms of their bioconcentration potential as compared with native vegetation at the site.

Laboratory and field investigations have shown that hybrid poplar trees can be established in mine tailings at a Superfund site without objectionable uptake of As and Cd into leaves. The laboratory study showed that estimates can be made easily and quickly regarding uptake and toxicity of metals. Field results demonstrated that the technology can be used at shallow contaminated sites for soil stabilization or in conjunction with other methods for closing a site.

Tri-State Mining Region

A number of studies have been made relating directly to vegetative remediation or to factors involved in establishing vegetation on contaminated soils or mine spoils in the Tri-State Mining Region. Several studies have dealt with a mine waste material known as chat, and one study examined a contaminated alluvial soil. Chat is a rock waste material generated from the initial processing of the metalliferous ore and consists primarily of rock fragments ranging in size from approximately 4 mm to clay sized ($<2\,\mu m$) and having Zn, Pb, and Cd concentrations as high as 43 750, 4500, and 160 $mg\,kg^{-1}$, respectively.[12] Chat piles are scattered throughout the area. The finer sized particles are selectively eroded away from the piles by wind and water and contribute to metal-enriched sediments and wind-blown dusts.

The Galena Superfund site consists of a large area that is nearly void of vegetation and contains numerous piles of chat and other waste materials. The remediation plan calls for using the piles of material to fill in mine shafts and other voids, recontouring to control run-off, and establishing vegetation to further control erosion and run-off.

An unbalanced factorial arrangement of organic waste amendments (composted yard waste, composted cattle manure, spent mushroom compost, and turkey litter); organic waste application rate (0, 22.4, 44.8, and $89.6\,Mg\,ha^{-1}$); and inorganic fertilizer rate (zero, a rate recommended for native grass establishment, and a rate recommended for establishment for a grass–legume mixture) was used to evaluate vegetative responses in a chat material seeded with a mixture of native

Table 4 The effect of organic waste source and and of fertilizer rate on plant density, species richness, and total cover after amendment of a zinc–lead chat tailing[42]

Main effect	Plant density/ plants m^{-2}	Species richness (number of species)	Total cover/%
Organic waste source[a]			
TL	15.6a[b]	6a	35a
CM	86.3b	26b	44b
MC	57.9c	16c	36ab
YW	61.5c	21bc	41ab
C	33.0d	9a	10c
Organic waste rate (mg ha^{-1})			
0	32.9a	9a	10a
22.4	53.7b	21bc	32b
44.8	54.4b	18b	40c
84.6	57.9b	25c ·	45c
Fertilizer rate[c]			
none	57.5a	22a	40a
NG	55.4a	20a	35a
GL	47.9a	20a	35a

[a]TL = turkey litter, CM = composted cattle manure, MC = spent mushroom compost, YW = composted yard waste, C = control

[b]Means within the same column and main effect followed by the same letter are not significantly different at the 0.05 level

[c]NG = rate recommended for establishment of native grasses, GL = rate recommended for establishment of a grass–legume mixture

and tame grasses and leguminous forbs.[42] Table 4 shows the effects of organic waste source, organic waste rate, and fertilizer rate on total plant density, species richness, and total cover after the initial growing season. All three response variables were increased significantly by the organic waste sources as compared with the control, with composted cattle manure generally providing the greatest increase and turkey litter giving the least increase. The poor performance of turkey litter as compared with the other organic waste sources was due to acidification caused by nitrification of ammoniacal nitrogen forms in the material. Significant increases were also evident with increasing rates of organic waste. The addition of fertilizer had little beneficial effect, however. The combined results suggested that merely supplying the primary plant nutrients (N, P, and K) is not sufficient for acceptable establishment of vegetation in this material. Although the organic waste materials increased plant-available N, P, and K as well, they also increased organic C levels, cation exchange capacities, and the concentrations of other secondary and micronutrients (data not shown). Any potential benefits with regard to alleviating Zn phytotoxicity are unknown. This work has been applied directly to the remediation efforts at the Galena Superfund site.

[42] M. R. Norland, Proceedings of the Association of Abandoned Mine Land Programs, Dept. of Natural Resources, Div. Environ. Qual., Jefferson City, MO, 1991, pp. 251–264.

Table 5 The influence of organic and inorganic fertilizers and mycorrhizal fungi on biomass production and in uptake by *Andropogon geradii* and *Festuca arundinacea* grown in chat[43]

| Mycorrhizal treatment | Fertilizer amendment | | | | | |
	none	NH_4	manure	KH_2PO_4	NH_4 and manure	Manure and KH_2PO_4
Biomass/g						
A. geradii[a]						
mycorrhizae	0.07bc	0.03c	0.08b	0.08b	0.41a	0.51a
no mycorrhizae	0.07bc	0.05bc	0.05bc	0.07bc	0.06bc	0.05bc
F. arundinacea						
mycorrhizae	0.07b	0.04b	1.04a	0.07b	1.43a	1.47a
no mycorrhizae	0.08b	0.07b	0.03b	0.07b	0.03b	0.06b
Zn uptake/mg plant^{-1}						
A. geradii[b]						
mycorrhizae	66c	nd	168bc	127bc	330ab	520a
no mycorrhizae	88c	78.8c	nd	75c	nd	95c
F. arundinacea						
mycorrhizae	159c	120c	905b	167c	1827a	984b
no mycorrhizae	241c	119c	84c	186c	294c	133c

[a]Means for each plant species followed by the same letter are not significantly different (P = 0.05)
[b]nd = not determined because of insufficient root biomass

The role of mycorrhizal fungi in establishing vegetation in the chat material also has been studied.[43] Table 5 shows the effect of various amendments and mycorrhizal fungi on biomass production and Zn uptake by big bluestem [*Andropogon geradii* Vit.] and tall fescue [*Festuca arundinacea* Schreb.]. Big bluestem is an obligate mycotroph that requires mycorrhizae to grow in soils with low fertility, whereas tall fescue is a facultative mycotroph that grows well in low fertility environments in the absence of mycorrhizae. In this situation, additional biomass production occurred only when mycorrhizae were present with adequate nutrients, illustrating the importance of fungi in alleviating Zn toxicity to the plants. The exact mechanism for this is not known. It may be related to the binding of the metals in the rhizosphere by the fungi or a change in the metal binding capacity of the cell walls, both of which could act to increase plant resistance to Zn.

Figure 5 shows the effects of various soil amendments on changing Zn bioavailability and the resulting changes in soybean [*Glycine max* (L.) Merr.] tissue composition and yields in a metal-contaminated alluvial soil. This soil was collected approximately 125 m from the Spring River in the Tri-State mining region and was in a field under crop production. Soybeans growing on site were severely chlorotic, and Zn phytotoxicity was the suspected cause because of high Zn concentrations (1090 mg kg^{-1}) in soybean tissue samples collected there. No mining activity had occurred adjacent to the field and the source of the Zn was

[43] B. A. D. Hetrick, G. W. T. Wilson, and D. A. H. Figge, *Environ. Pollut.*, 1993, accepted.

Figure 5 Relationship between soybean tissue Zn concentrations and relative yield in a metal contaminated alluvial soil. The variation in tissue Zn concentrations was a result of changes in soil bioavailable Zn levels induced by various soil amendments without changing the total Zn concentration[7]
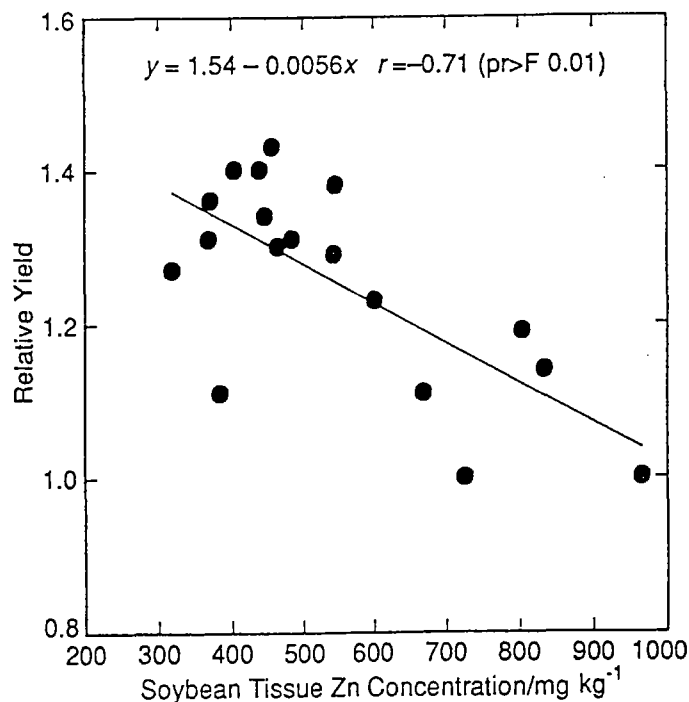
metal-contaminated sediments deposited during periodic flooding events. The amendments were lime, P, cattle manure, sewage sludge, poultry litter, or various combinations of lime and cattle manure. The amendments produced KNO_3^- extractable Zn concentrations from 3.7 to 63.3 mg kg^{-1} with a corresponding range of soybean tissue Zn concentrations of 318 to 1153 mg kg^{-1}. Soybean yields were influenced by the changes in tissue Zn concentrations with a range of 1.0 to 1.4 (Figure 5). The manipulation of bioavailable Zn levels was done without changing the total Zn concentration of the soil. Although the overall thrust of this project was not vegetative remediation, it is one of the few studies that provides data on soil chemical changes induced by soil amendments designed to reduce metal bioavailability.

Studies have shown that various amendments and mycorrhizal fungi aid in enhancing plant growth in contaminated soils and mine spoils from the Tri-State Mining Region. As a result, a vegetative remediation strategy is being used at the Galena Superfund site as part of the overall clean-up effort. Additional information has been obtained regarding the importance of mycorrhizae for plant growth under Zn toxic conditions and on the usefulness of soil chemical fractionation schemes in assessing soil chemical changes induced by amendments.

5 Modeling of the Fate of Heavy Metals in Vegetated Soils

The root–soil water transfer process is a major part of the sub-surface hydrologic system. The development of quantitative models that describe water movement in the root–soil environment has been reviewed.[10] The Leaching Estimation and

Chemistry Model, LEACHM, has been used to simulate the movement of water and solutes through both layered and non-layered soil profiles.[44] A coupled root–soil water flow model that includes the vertical movement of water through the root system has been developed.[45,46] Soil water movement in the vertical and horizontal directions of a non-homogeneous variably saturated soil can be simulated with this model.

Some of the processes that occur in the soil–root environment are limited by the rate of diffusion or reaction and kinetic models should be used rather than the equilibrium models described earlier. Diffusion within solids is slow; it is often an important consideration when modeling the leaching of metals in soil.

Two important considerations in modeling the fate of metals in the root–soil environment are the uptake into the plant and the impact of root exudates on pH and leaching. Because micro-organisms degrade root exudates, any modeling of the impact of the organic ligands on metal leaching should include a root exudate and a microbial population balance.[47]

When the behavior of the solute is modeled with an equilibrium model, two distinct cases can be considered. Below the solubility limit, the metal will not precipitate, and a precipitated solid phase will not be present. On the other hand, when a precipitated solid phase is present, the solute concentration will be at the solubility limit and will remain at that value until all of the solid phase is dissolved. In this case, a model for the solid phase is needed to simulate the dissolution process and follow the transient behavior of the mass of precipitated metal. In the model that follows, the first case is considered.

As discussed previously, a variety of factors govern the fate of heavy metals in a vegetated soil; however, providing detailed mathematical expressions describing all of these processes would produce a nearly intractable problem. Thus, a somewhat simplified approach will be employed for developing a method to predict the fate of heavy metals in a rooted soil. Figure 6 depicts the conceptual approach used in development of the fate and transport model. It is assumed that the primary mechanism for metal transport through a soil is water movement, with losses or additions of metals to the soil–water occurring from four sources: (1) uptake into the vegetation's root system by plant transpiration; (2) adsorption onto the vegetation's root system; (3) bonding to exchange sites on inorganic soil constituents; and (4) adsorption to insoluble soil organic matter.

A model that has been shown to provide an accurate depiction of the movement of water in the presence of a transpiring crop's root system can be described as:[45,46]

$$\frac{\partial}{\partial z}\left[K_s \frac{\partial(\psi_s + z)}{\partial z}\right] - q = \left[\beta S_s + S_y \frac{dS_c}{d\psi_s}\right]\frac{\partial \psi_s}{\partial t} \tag{1}$$

[44] R. J. Wagenet and J. L. Hutson, 'Leaching Estimation and Chemistry Model, Version 2.0, A Process Based Model of Water and Solute Movement, Transformations, Plant Uptake, and Chemical Reactions in the Unsaturated Zone', *Continuum*, Vol. 2, Water Resources Institute, Cornell University, Ithaca, NY, 1989.

[45] M. A. Marino and J. C. Tracy, *J. Irrig. Drain. Eng.*, ASCE, 1988, **114**, 588–604.

[46] J. C. Tracy and M. A. Marino, *J. Irrig. Drain. Eng.*, ASCE, 1989a, **115**, 608–625.

[47] L. C. Davis, L. E. Erickson, E. Lee, J. F. Shimp, and J. C. Tracy, *Environ. Prog.*, 1993, **12**, 67.

Figure 6 Schematic representation of the modeling approach
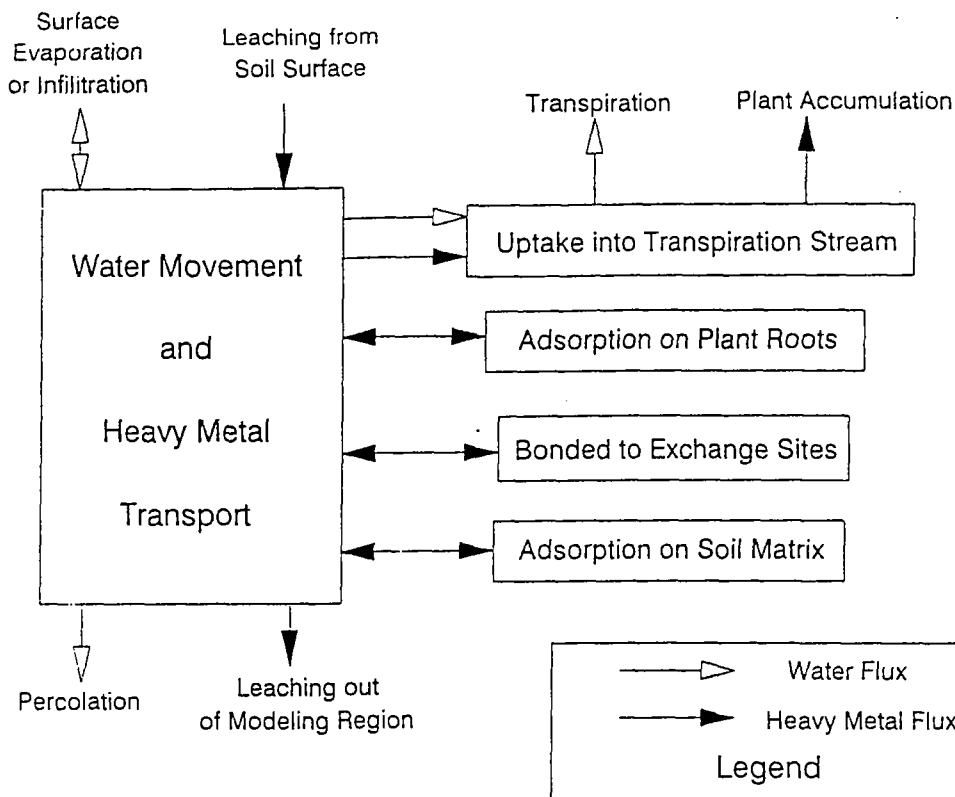
$$\frac{\partial}{\partial z}\left[K_r\frac{\partial(\psi_r + z)}{\partial z}\right] + q = R_d\frac{\partial WC_r}{\partial t} + WC_r\frac{\partial R_d}{\partial t} \tag{2}$$

in which z is the vertical direction in the soil; K_s is the hydraulic conductivity of the soil in the vertical direction; K_r is the hydraulic conductivity of the root in the vertical direction; ψ_s is the soil–water pressure head; ψ_r is the root–water pressure head; S_y is the specific yield of the soil; S_s is the specific storage of the soil; $\beta = 0$ if $\psi_s < 0$ and $\beta = 1$ elsewhere; WC_r is the root–water content, a function of the root–water pressure head; R_d is the root density in the soil; t equals time; $S_e = \theta/n$ which is the effective saturation of the soil, where θ is the soil–water content and n is the soil porosity; and q equals the rate at which soil–water is extracted by the plant's root system per unit volume of soil, defined as:

$$q = S_e R_d \Gamma(\psi_s - \psi_r) \tag{3}$$

where Γ is a lumped parameter representing the permeability of a plant's root system.

Equations (1) through (3) represent a coupled set of partial differential equations that can be solved numerically, given that the root parameters, the soil characteristics, the initial conditions, and boundary conditions are known.

The solutions of equations (1) through (3) describe the distributions of the water flux throughout the soil profile. Thus, Darcy's law is employed to calculate the water flux, V, distribution based on the soil–water pressure heads, such that:

$$V = -K_s\frac{\partial(\psi_s + z)}{\partial z} \tag{4}$$

The transport of heavy metals through the soil profile can then be described

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using the water flux distribution and the advection–dispersion equation, as:

$$\frac{\partial}{\partial z}\left[\theta D \frac{\partial C}{\partial z} - VC\right] - q_m + S = \frac{\partial}{\partial t}[C(\theta + K)] \tag{5}$$

in which C is the concentration of heavy metals in the soil–water; D is the macrodispersion coefficient for heavy metals in the soil; q_m is the uptake of heavy metals by roots into the plant transpiration stream; S is the sink/source of contaminants across modeling boundaries; and K equals a lumped parameter accounting for the adsorption onto root and soil surfaces and ion exchange.

Several heavy metals are necessary as plant nutrients (*e.g.* Cu and Zn)[48] and a significant fraction of these metals can be taken up by the roots during plant transpiration. However, other metals are toxic to some plant species and a larger fraction of these metals are excluded during the root uptake process. Thus, development of the uptake term, q_m, in equation (5) will have to be based on the specific plant type and metal being studied, and very few generalizations can currently be made about this process. Nonetheless, a general model that may be useful for developing a mathematical simulation model of this process is similar to a proposed model[49] for the uptake of organic chemicals into a plant's transpiration stream, simulated as a linear function of root water uptake, so that:

$$q_m = f_u q \tag{6}$$

where f_u equals the ratio of the concentration of the chemical in the root water to the concentration in the soil water. Use of this expression for metals in conjunction with equation (3) would allow the uptake to be calculated as:

$$q_m = f_u R_d S_e \Gamma(\psi_s - \psi_r) \tag{7}$$

where f_u would have to be calibrated as a site-specific parameter.

The lumped parameter, K, in equation (5) actually accounts for three processes: (1) adsorption to the root mass; (2) adsorption to the soil matrix; and (3) ion exchange. Very little information is available to quantify these relationships based on the general characteristics of a site. However, it is felt that a reasonable approximation would be to assume that the heavy metals partition into each phase (water, root, soil, and biomass) in a linear fashion and that the time frame of the simulations is of long enough duration to assume equilibrium conditions. In this fashion, the lumped adsorption parameter, K, can be described as:

$$K = \rho k + R_d k_r + k_e E \tag{8}$$

in which ρ is the soil density; k equals the linear partition coefficient between the soil–water and soil matrix; k_r is the linear partition coefficient between the soil–water and the root mass; k_e is the linear partition coefficient between the soil–water and the ion exchange sites on the solid phase; and E is the cation exchange capacity of the soil.

The concentration C includes all forms of the metal dissolved and suspended in the soil–water, and can be written in terms of its components: C_1, the

[48] A. J. Friedland, in 'Heavy Metal Tolerance in Plants: Evolutionary Aspects', ed. A. J. Shaw, CRC Press, Boca Raton, FL, 1989, pp. 7–20.
[49] G. G. Briggs, R. H. Bromilow, and A. A. Evans, *Pestic. Sci.*, 1982, **13**, 495–504.

concentration of the charged species; C_2, the concentration of metal complexed with an inorganic species, A_2; and C_3, the concentration of metal complexed with organic species, A_3.

The total concentration, C, can then be expressed in terms of C_1 as:

$$C = C_1 + K_2 A_2 C_1 + K_3 A_3 C_1 \tag{9}$$

where K_2 and K_3 are the partition coefficients associated with the metal complexed with the inorganic and organic species, respectively.

If the ion exchange process involves only the charged species C_1, then equation (5) may be written in the form:

$$\frac{\partial}{\partial z} \left[\theta D \frac{\partial [C_1(1 + K_2 A_2 + K_3 A_3)]}{\partial z} - V C_1(1 + K_2 A_2 + K_3 A_3) \right] - f_u R_d S_e \Gamma(\psi_s - \psi_r) + S$$

$$= \frac{\partial}{\partial t} [C_1(1 + K_2 A_2 + K_3 A_3)(\theta + \rho k + R_d k_r) + C_1 k'_e E] \tag{10}$$

It is likely that the root exudate concentration, rhizosphere biomass density, and root density probably will be variable over time. Thus, some mechanism of predicting these densities as they vary in relation to the time of year, climatic conditions, and general site conditions must be employed. However, such models will not be included here due to the limited scope of this paper.

The estimation of the soil matrix partition coefficient, k, in equation (8) also must be done on a site-specific basis and will depend on factors such as the soil's organic content and pH. With the introduction of vegetation at a site, both the organic content and the pH of the soil could change significantly and, thus, the partition coefficient must be described as a function of both, such that:

$$k = f(\mathrm{pH}, \%Oc) \tag{11}$$

where $\%Oc$ is the percent organic matter in the soil matrix. In most cases it should be possible to develop this relationship on a site specific basis. However, a method also would have to be developed to predict the pH and organic content of a soil once vegetation has been introduced, which could prove difficult.

The model governing the fate and transport of a heavy metal can be solved numerically. The model solutions could then proceed by solving equations (1) through (3) to determine the water pressure distribution in the soil profile, then solving equation (4) to calculate the soil–water flux distribution. Finally, equation (10) could be solved using the soil–water flux and root water extraction calculations to determine the heavy metal concentration of the soil–water in the soil profile for each time increment during the simulation period. Equation (10) also could be solved simultaneously with the balances for root exudates and microbial biomass, if transient changes in root exudate concentration, A_3, are to be included in the model.

One of the challenges of using mathematical models to simulate the fate of heavy metals in soils is to collect sufficient equilibrium and soil characterization data. Although some data for root exudates has been collected,[50] more research

[50] A. P. Schwab and M. K. Banks, Proceedings of the 86th Annual Meeting and Exhibition of the Air and Waste Management Association, Denver, CO, June 14–18, 1993, Paper 93-WA-8906.

is needed before the model could be utilized to design a vegetative remediation scheme. However, the proposed model can be used to demonstrate the qualitative effects that the introduction of vegetation would have on soils contaminated with heavy metals.

Equations (1) and (2) simply describe the water flow regime in a variably saturated soil, with equation (4) providing a calculation of the water flux and equation (3) representing the amount of water extracted by a plant's root system. Any transpiration by vegetation introduced into a barren soil would result in the extraction of soil–water by plant roots. This would have two significant effects on the transport of heavy metals through a soil. First, the water sink provided by the plant roots generally would be strongest in areas with the largest root densities, typically near the soil surface. This would decrease the downward rate of water flow through the soil, thereby decreasing the mass of heavy metals leached below the root zone. Second, the water sink provided by the root system also would reduce the overall soil–water potential, ψ_s, which in turn would lower the soil–water content. Then, because the hydraulic conductivity of a soil decreases with decreasing soil–water content, the presence of the plant's root system also would decrease soil permeability, further restricting the movement of water and metals. Thus, equations (1) through (4) tell us that the introduction of a vegetative system to a heavy metal-contaminated soil would result in a type of hydraulic containment system.

Equation (5) describes the fate and transport of heavy metals through the soil profile. The advective and dispersive terms, V and D, are related to the movement of water. Equations (6) and (7) describe the uptake of heavy metals by a plant's root system. Because of their formulation, some metals probably would be taken up during the root–water uptake process described in equation (3), thereby reducing the mass of heavy metals in the soil profile. Thus, the introduction of vegetation would result in a reduction in the mass of heavy metals in a soil. However, the heavy metals that are taken up would accumulate in the plant biomass, typically in plant leaves. If the vegetative system were left unmanaged, plant dormancy at the end of a growing period would result in the decomposition of parts of the plant and the introduction of the heavy metals back into the soil at the soil surface where the leaves and other matter would fall, thus producing a source of metals, defined by the term S in equation (5). For the uptake to provide a true sink of heavy metals in the soil system, the vegetation would have to be managed in some way, such as harvesting, to prevent the reintroduction of the metals into the soil profile.

Equations (8) through (11) describe the adsorption of heavy metals to the organic and inorganic matter in the soil matrix. In general, heavy metals tend to adsorb readily to organic matter. The introduction of vegetation at a site would produce an increase in organic matter from the soil matrix to the plant's root system and the microbial mass associated with the plant's rhizosphere. Equation (8) thus indicates that the introduction of vegetation in a soil would decrease the mobility of the heavy metals, thereby providing a better containment system. However, most plant roots produce root exudates, so that a healthy environment is maintained in the rhizosphere for microbial and root growth. This property tends to alter the pH of a soil, so that root growth can be maintained at optimal

levels, with pH values in the range of 6 to 8 favoring most plants.[51] If the natural pH of the contaminated soil is above these levels, the introduction of vegetation could result in a substantial lowering of the pH. This could reduce the partition coefficients in equation (9) and result in the metal becoming more mobile in the soil. In situations where the soil pH is below 8, soil amendments could be utilized to maintain a relatively constant pH, thus preventing an increase in the heavy metal mobility once the vegetative containment system is fully developed.

The modeling results that could be expected for the development of a vegetative remediation system would be extremely site dependent. However, the overall analysis of the model presented above suggests that, for many heavy metal contaminated soils, vegetation should provide a positive influence for enhancing the on-site containment of the metals and the possible removal of a portion of the metals through the harvesting of the vegetation.

6 Conclusions

Numerous remediation options exist for metal-contaminated sites. These range from complete excavation of contaminated material accompanied by some treatment to *in situ* encapsulation and to vegetative remediation. Vegetative remediation is aesthetically pleasing and it offers several advantages, including the minimization of erosion, low cost as compared with other remediation options, and the potential to reduce net percolation through contaminated sites. Amendments to contaminated soil or mine spoil materials may reduce metal uptake by plants by reducing metal bioavailability. Theoretically, such amendments likely reduce free metal ion activities in the soil solution although it is difficult to estimate or measure the actual treatment effects. On a more practical basis, chemical fractionation schemes are useful for quantifying treatment efficacy. Mycorrhizal fungi play an important role in establishing vegetation by allowing plants to utilize plant nutrients more efficiently and by decreasing plant sensitivity to phytotoxic metal concentrations. Thus, more contaminated areas may be suitable for vegetative remediation than was previously believed.

The use of trees holds particular promise for vegetative remediation. In addition to providing erosion protection, they have the potential to transpire considerable amounts of water compared to non-woody plant species. This may help in reducing the downward migration of contaminants. Trees can also produce biomass for chemical and/or energy use. Initial results suggest that food-chain transfer of contaminants due to uptake into leaves and stems is not a concern.

A model has been presented that can estimate the effects of vegetation on the fate of metals in contaminated soils and mine spoils provided the appropriate parameters can be obtained. The model takes into account root and soil characteristics, water balance, and the influence of vegetation on certain soil chemical properties with time. Use of the model would allow a more thorough appreciation and understanding of vegetative remediation.

[51] G. B. Tucker, W. A. Berg, and D. H. Gentz, in 'Reclaiming Mine Soils and Overburden in the Western United States: Analytical Parameters and Procedures', ed. R. D. Williams and G. E. Schuman, Soil Conservation Society of America, Ankeny, IA, 50021, pp. 3–26.

Acknowledgements

Using Poplar Trees as a Landfill Cover:

Experiences with the Ecolotree™ Cap

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Abstract

The Ecolotree™ Cap is a new alternative for covering landfills that offers significant economic and environmental advantages over traditional capping methods. The Ecolotree™ Cap features a stand of fast-growing hybrid poplar trees that quickly establish a dense canopy and deep rooting system. The trees and vegetation prevent precipitation from entering the landfill through two processes. First, the canopy intercepts rainfall and reduces the amount reaching the ground surface. Second, the moisture that does enter the ground is extracted from the root zone during plant respiration. Water that falls on the cap during the non-growing season is stored in the engineered cap soil system for use during the following growing season. The Ecolotree™ Cap system saves money, saves energy, and produces a marketable product with value for the economy and the environment. Ecolotree systems have been installed in a variety of applications in the United States and abroad.

tree root systems. In moist climates with year-round precipitation, it may be possible to discontinue irrigation after two growing seasons. In arid climates or regions with low rainfall during the growing season, it may be necessary to continue supplemental irrigation for a longer period. In some instances, this offers an opportunity for on-site utilization of landfill leachate.

Once the trees are established, the system operates with relatively low maintenance. Plant health monitoring and occasional pruning and thinning of the tree population are the primary maintenance functions. Monitoring of soil moisture is also valuable to document system performance. In most cases, this can be automated.

Ecolotree™ Cap Design

There are three key components of the Ecolotree™ Cap:

- <u>A thick cover of soil and soil amendments</u> - Such as compost, ground wood, chopped paper, raw or digested sewage sludge, lime sludge, manure, paper mill waste, and other organic biomass. The water-holding layer acts as a sponge to hold water in soil pores. The surface soil stores water within the root zone. During respiration, the plants uptake water through their extensive root systems. Dewatering creates pore spaces that provide precipitation storage. Due to the large soil volume associated with the deep rooting and robust water uptake, the system is an effective means to manage infiltration and soil moisture.

- *Populus spp. (poplar) trees and grasses/ legumes* - These plants grow dense, deep roots into the landfill cover soil, thus acting as a pump that transpires the soil water back to the atmosphere. The plant uptake, driven by solar-powered photosynthesis, removes water and nutrients from root zones, which reach predictable depths greater than 1.5 m (5 ft) in upland soils.

- <u>Planting technique</u> - Cap installation includes growing planting stock; harvest, processing, storage, and quality control of cuttings; transport; destination storage; pre-plant tillage; planting; nutrition; vector control; plant maintenance; equipment management; and regulatory permitting.

Contrast and Compare: Ecolotree™ Cap and EPA Approved Landfill Cover

The U.S. Environmental Protection Agency (EPA) has approved clay or geomembrane covers as landfill covers. These low permeability layers are designed as a 'raincoat' barrier with precipitation running off and with slight regard for plant growth. The Ecolotree™ Cap focuses on re-establishing a vigorous ecosystem that uses or stores water in the root zone. The poplar/grass plant system grows faster than most alternative crop schemes and has the physiological capacity to consume more water than falls by precipitation.

When the survival, growth rate, and rooted soil depth are predictable, the transpiration of water is predictable. Conservatively, plants remove 600 liters of water from the soil pores for every kilogram of stem dry matter growth. The leaves transpire this ground water back to the atmosphere as water vapor. When transpiration exceeds rainfall, plants remove stored water from the rooted cover soils. This dehydrating action effectively gives the cover a water storage capacity during winter dormancy. An engineered soil cap with enough depth and water holding capacity can store all non-growing season water without deep percolation for consumption by the trees during the following growing season.

Buffer features a crop of hybrid poplar trees combined with a grass ground cover. The surface runoff and leachate are collected and stored in a 10-million-gallon lined lagoon. During the irrigation season of April through September, the wastewater is applied to the Ecolotree™ Buffer with an automated irrigation system. The trees are purposely deficit irrigated to ensure that irrigation water is not leached through the root zone. Irrigation is ceased prematurely in September in order to force the trees to deplete the remaining moisture in the soil prior to the wet winter season. This results in capacity for the soil to store seasonal rainfall during the winter months.

Barje Landfill

The Barje Landfill is a municipal and industrial waste landfill operated by the City of Ljubjana in Ljubljana, Slovenia. A 10-acre prototype Ecolotree™ Cap was planted in 1993 and 1994 with the primary goal of protecting ground water by reducing leachate through the wastes. Installation and technical support for the system is being supplied by Slovenian technicians and scientists. The Ecolotree™ Cap offers the secondary benefits of improved aesthetics, wildlife habitat and biomass production. The wood will be used in an existing market for many products used locally or exported.

Virginia Landfills

The Virginia Department of Environmental Quality (DEQ) is interested in evaluating the Ecolotree™ Cap for consideration as a possible alternative to conventional Subtitle D landfill caps in the Commonwealth of Virginia. At least four feasibility studies will be conducted to evaluate the application of the Ecolotree™ Cap to specific Virginia landfill sites in various climatic zones. It is anticipated that the feasibility studies will lead directly to the design and installation of at least four prototype Ecolotree™ Cap installations. The purpose of the feasibility studies and prototype installations is to develop criteria and regulatory procedures that would allow the Virginia DEQ to properly evaluate and guide the use of the cost-effective and environmentally friendly system.

Union Electric

Union Electric Company operates the Meramec Power Plant, a coal-fired power generation plant in St. Louis, Missouri. Fly ash produced as a byproduct of the combustion process is deposited with sluice water in a waste storage pond. Union Electric is currently planning closure of a number of fly ash ponds at the plant, which have been filled to capacity. The Ecolotree™ Cap is being evaluated for closure of these fly ash ponds as an alternative to a cap featuring a synthetic geomembrane. The Ecolotree™ Cap appears to offer significant advantages over the geomembrane will be evaluated in this study. Conceptually, the composition of the fly ash does not appear to vary significantly from many naturally occurring soils. Therefore, it is anticipated that with the proper amendments for balanced plant nutrition, the fly ash will offer a suitable matrix for poplar tree growth. A 6-acre demonstration site is being installed in 1995.

Johnson County Landfill

The Johnson County Landfill, located in Iowa City, Iowa, was closed before the Subtitle D regulations were in effect. In 1992 and 1993, a 9-acre Ecolotree™ Cap and perimeter buffer were installed to stabilize and revegetate this landfill.

wastewater, a subsurface drainage system will be installed to capture water leaching beyond the root zone.

Woodburn WWTP

The Woodburn Wastewater Treatment Plant (WWTP) in Woodburn, Oregon, uses a rotating biological contactor (RBC) to provide advanced secondary treatment of domestic and industrial wastewaters. Effluent produced by the plant is currently discharged to the Pudding River, which has been designated as Water Quality Limited by the Oregon Department of Environmental Quality (DEQ). Due to the Water Quality Limited designation, the DEQ revised the treatment requirements for wastewater treatment plants discharging to the Pudding River. As a result, the City of Woodburn is required to upgrade its existing secondary treatment facilities with tertiary treatment prior to effluent disposal.

The installation of an Ecolotree™ Buffer has been identified as a possible alternative for meeting this requirement. A 10-acre demonstration site is being designed to establish the design criteria for a full-scale Ecolotree™ Buffer installation. The 10-acre prototype installation will feature land application of effluent from the secondary treatment system. An irrigation system with low-pressure, mini-sprinklers will be used to irrigate the tree/grass ecosystem. Design variables to be tested at the site include various poplar tree clones, tree planting densities and irrigation loading rates. The system will be closely monitored to document performance of the system. The monitoring effort will include climatic data, soil moisture measurements throughout the tree rooting zone, quantity and quality of wastewater, quality of soil water, plant tissue analyses and soil analyses for nutrients and waste stream constituents.

Phytoremediation of Organic and Nutrient Contaminants

Pilot and full-scale studies are demonstrating the promise and limitations of using vegetation for remediating hazardous wastes in soils and sediments.

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Phytoremediation, the use of vegetation for the in situ treatment of contaminated soils and sediments, is an emerging technology that promises effective and inexpensive cleanup of certain hazardous waste sites. The technology has already been shown to be effective in a number of full-scale and pilot studies. Phytoremediation is most suited for sites with shallow contamination (< 5 m depth); moderately hydrophobic pollutants such as BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), chlorinated solvents, or nitrotoluene ammunition wastes; or excess nutrients (nitrate, ammonium, and phosphate).

Because phytoremediation is still in development, the techology is not yet widely accepted by regulatory agencies and therefore not commonly used. In addition, phytoremediation may take longer than traditional approaches to reach cleanup goals or may be limited by soil toxicity. However, as a rule, plants will survive higher concentrations of hazardous wastes than will most microorganisms used for bioremediation.

A potential application of phytoremediation would be bioremediation of petrochemical spills and contaminated storage areas, ammunition wastes, fuel spills, chlorinated solvents, landfill leachates, and agricultural nonpoint source runoff (i.e., pesticides and fertilizers). Generally, phytoremediation is used in conjunction with other cleanup approaches.

Plants remediate organic pollutants via three mechanisms: direct uptake of contaminants and subsequent accumulation of nonphytotoxic metabolites into plant tissue; release of exudates and enzymes that stimulate microbial activity and biochemical transformations; and enhancement of mineralization in the rhizosphere (the root-soil interface), which is attributable to mycorrhizal fungi and the microbial consortia. It is also possible to concentrate metals in higher plants, and phytoremediation includes the use of plants to remediate sites contaminated by metals. However, in this article we focus on organic and nutrient pollutants.

Vegetation offers other benefits at contaminated sites; phytoremediation increases the amount of organic carbon in the soil which, in turn, stimulates microbial activity. In addition, the establishment of deep-rooted vegetation helps to stabilize soil. When windblown dust is controlled, it reduces an important pathway for human exposure via inhalation of soil and ingestion of contaminated food. Plants also transpire considerable amounts of water. This loss of water can reverse the downward migration of chemicals by percolation and can lead to absorption of surface leachate.

Figure 1 shows a schematic of mass flow through a woody, flood-tolerant tree species. (Oxygen, water, and carbon transport mechanisms vary among plant species.) Plants supply oxygen to the soil rhizosphere; for example, seedlings in the laboratory can transport considerable quantities of oxygen to roots in the rhizosphere (0.5 mol O_2 per m^2 of soil surface per day) (1). However, roots also demand oxygen for respiration and, therefore, the total effect of dense root systems needs to be considered in the engineering design. The figure also demonstrates how plants are able to take up contaminants directly from the soil water and release exudates that help degrade organic pollutants via co-metabolism.

Direct uptake of organic pollutants

Direct uptake of organics by plants is a surprisingly efficient removal mechanism for moderately hydrophobic organic chemicals (octanol–water partition

Researcher measures one season of growth of hybrid poplar tree being used as a riparian zone buffer at Amana, IA.

coefficients, log K_{ow} = 0.5–3) in shallow contaminated sites. These include most BTEX chemicals, chlorinated solvents, and short-chain aliphatic chemicals. Hydrophobic chemicals (log K_{ow} > 3.0) are bound so strongly to the surface of roots that they cannot easily be translocated within the plant, and chemicals that are quite water soluble (log K_{ow} < 0.5) are not sufficiently sorbed to roots or actively transported through plant membranes (2).

Once an organic chemical is taken up, a plant can store the chemical and its fragments in new plant structures via lignification; or it can volatilize, metabolize, or mineralize the chemical all the way to carbon dioxide and water. Detoxification mechanisms may transform the parent chemical to non-phytotoxic metabolites, including lignin, that are stored in various places in plant cells.

The direct uptake of a chemical through the roots depends on the plant's uptake efficiency and transpiration rate as well as the concentration of the chemical in soil water. Uptake efficiency, in turn, depends on physical–chemical properties of the contaminant, chemical speciation, and the plant itself (plants vary in the transporting agents they use to take up organic contaminants). Transpiration is a key variable that determines the rate of chemical uptake for a given phytoremediation scheme—it depends on the plant type, leaf area, nutrients, soil moisture, wind conditions, and relative humidity.

Enzymes and exudates

Plants may release to the soil environment exudates that help degrade toxic organic chemicals. Leakage of exudates (sugars, alcohols, and acids) from the plant can amount to 10–20% of plant photosynthesis on an annual basis (3).

For example, in work at the University of Iowa we characterized the molecular weight distribution of organic exudates from the root systems of hybrid poplar trees. Dissolved organic carbon concentrations were substantial: 10–120 mg L^{-1}, with a median molecular weight of 1100 daltons and 1–10 mg L^{-1} of acetic acid (acetic acid is a good substrate for soil microorganisms).

We also examined enzyme reactions in plant sediment, plant soil, and exudate systems. Wherever we have found significant natural activity in the transformation of contaminants mixed with sediment and soil, we have isolated plant enzymes as the causative agent. In studies at EPA's laboratory in Athens, GA, five enzyme systems—dehalogenase, nitroreductase, peroxidase, laccase, and nitrilase—have been identified. Tracing natural indigenous processes exclusively to plants provides strong evidence of the po-

FIGURE 1

Oxygen, water, and chemical cycling through a tree

Phloem
photosynthates + O_2

Xylem
H_2O +
nutrients

tential for phytoremediation and indicates that the future development of innovative phytoremediation must revolve around discovering which enzyme systems will degrade chemicals of concern. Table 1 specifies some plants and associated enzymes that degrade organic chemicals.

Through the use of rigorous mass balances and pathway analyses we have shown that nitroreductase and laccase enzymes break down ammunition wastes (2,4,6-trinitrotoluene or TNT) and incorporate the broken ring structures into new plant material or organic detritus that becomes a part of sediment organic matter. Another plant-derived enzyme, dehalogenase, helps reduce chlorinated solvents such as trichloroethylene (TCE) to chloride ion, carbon dioxide, and water. Determination of each of the metabolites, pathways, and reaction kinetics through dynamic mass balances and radiolabeled studies

provides vital information for ecological engineering that we hope will replace a trial-and-error selection of plants. A thorough understanding of pathways and end products of enzymatic processes also simplifies toxicity investigations of in situ phytoremediation.

Although isolated enzymes such as nitroreductase rapidly transform substrates such as TNT, our experience indicates that remediation should involve whole plants. Isolated enzymes are destroyed and inactivated by low pH, high concentrations of metals, and bacterial toxins. When plants are grown in soil or sediment slurries, pH is neutralized, metals are biosorbed or chelated, and enzymes remain protected inside the plant or sorbed to plant surfaces.

In our studies of TNT breakdown, plants such as hornwort increased pH from 3 to 7, sorbed high concentrations of metals that would usually inhibit bacteria, and remained healthy and viable. Overall, plants can accommodate mixed wastes (organic and metals) and other harsh conditions.

Rhizosphere biodegradation

Anderson et al. (4) have demonstrated the importance of biodegradation in the rhizosphere. Plants help with microbial transformations in the rhizosphere in many ways.

Roots harbor mycorrhizae fungi, which metabolize organic pollutants. These fungi, growing in symbiotic association with the plant, have unique enzymatic pathways that help to degrade organics that could not be transformed solely by bacteria.

Plants supply exudates, which stimulate bacterial transformations and build up the organic carbon in the rhizosphere. In addition, the rapid decay of fine-root biomass can become an important addition of organic carbon to soils. The additional organic carbon, in turn, increases microbial mineralization rates. The increase in carbon also serves to retard organic chemical transport into groundwater. Moreover, we have found that microbial mineralization of atrazine is directly related to the fraction of organic carbon in the soil (5).

Finally, plants provide habitat for increased microbial populations and pump oxygen to the roots, a process that ensures aerobic transformations near the root that otherwise may not occur in the bulk soil. Microbial assemblages are abundant in the rhizosphere. Typical communities comprise 5×10^6 bacteria, 9×10^5 actinomycetes, and 2×10^3 fungi per gram of air-dried soil; bacteria live in colonies that cover as much as 4–10% of the plant root surface area (1, 6).

Applications of phytoremediation

Each cleanup situation requires a different plant or a number of plants in tandem. Alfalfa has been used for its nitrogen-fixing ability and deep rooting. Rye grass and fescue offer dense cover crops, often below a woody species. Trees of the *Salicaceae* family (willow and poplar) have been planted at several locations because of their flood tolerance and fast growth. Parrot feather and Eurasian water milfoil have been applied in aquatic mesocosms to break down ammunition wastes.

For example, in a cooperative pilot test with Au-
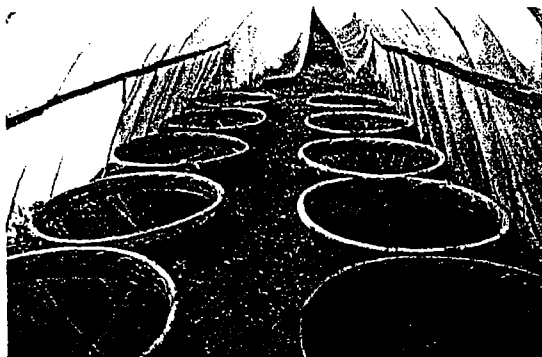
Photo 1. Mesocosm studies of TNT-contaminated soil: Studies conducted at the Army Ammunition Plant (Childersburg, AL) with 1 in. of TNT-contaminated soil (5000 ppm). Red color in the left front container (control) was the result of photolysis of TNT; most TNT remained in the control, which was still toxic to snails and tadpoles. The right front container was treated with parrot feather aquatic plants. The dark brown indicates degradation of the TNT; more than 90% removal occurred after 7 days, and toxicity was lowered.

Photo 2. Four years of growth in a riparian zone buffer strip: Four rows of hybrid poplar trees make a 25-ft buffer along a stream in Amana, IA, that decreases nutrients, sediment, and pesticides.

burn University, parrot feather was introduced into flooded mesocosms of TNT-contaminated soil. Rather than selecting plants by trial and error, we tested parrot feather from the site and detected the enzyme nitroreductase. At 5000 ppm of TNT, the contaminated soil was essentially sterile. In the initial sampling after one week, dissolved TNT concentrations decreased from 128 ppm (saturation) to 10 ppm. The disappearance of TNT attributable to parrot feather was rapid enough to support snails and tadpoles (Photo 1). However, new roots grew only along the edge of the contaminated soil, avoiding hot spots while breaking down the dissolved TNT in the water column.

Another plant system, hybrid poplar trees, offers some distinct advantages for treatment of contaminated soils with organic chemicals. These hybrid varieties are perennial, long-lived (25–50 years), fast growing, hardy, and tolerant of organics. Hybrid poplars grow easily from long cuttings planted deeply and can be harvested and regrown from the cut stump.

We have planted Imperial Carolina hybrid poplars (*Populus deltoides nigra*, DN34) from 2-m cuttings that have preformed root initials for rooting all along the buried depth (1.7 m). In dry years, roots will reach down toward the water table, establish-

ing a dense root mass that will take up large quantities of water. This process increases soil suction and decreases downward migration of pollutants. In the dormant season, there may be some leakage of water through the system, but normally precipitation is not great during this period.

In good soils and temperate conditions, the trees can grow 2 m in the first growing season and reach a height of 5–8 m after three years. We plant at a density of 10,000 trees per hectare, but the trees naturally thin themselves to about 2000 trees per hectare after several years. Average carbon fixation in the early years is 2.5 kg m^{-2} yr^{-1}. In Amana, IA, hybrid poplar trees planted along a riparian zone for six seasons have produced an average of 12 tons of dry matter per acre per year.

To control agricultural runoff along a small creek in prime Iowa agricultural land (Photo 2), hybrid poplars were planted in four rows as a riparian zone buffer strip (8 m wide, 10,000 trees per hectare). The goal was to intercept and remove atrazine and nitrate pollutants before they were delivered to the creek and surficial groundwater. Nitrate in surficial groundwater dropped from 50–100 mg L^{-1} to < 5 mg L^{-1} as nitrate. Also, in a related small pilot study, we found that 10–20% of the applied atrazine was taken up by the trees (7, 8).

Poplar trees make an excellent cap and closure at municipal landfills. In collaboration with an engineering consulting firm, 10,000 trees per hectare were planted as the final cap on a landfill at Beaverton, OR. Photo 3 shows the side slope of the landfill before planting and after one year of growth. Treatment of organic wastes is not the main goal at this site; rather, it

TABLE 2

Applications of phytoremediation at contaminated sites

Location	Application	Contaminants	Site results	Reference
Amana, IA	Nonpoint source control of ml stream with poplars	NO3, atrazine, alachlor, soil erosion	NO3 and 0, 10–20% atrazine were removed	1, 4, 7, 9, 10
Amana, IA	Municipal solid waste compost land application on poplars, corn, fescue	BEHP, B(a)P, PCB, chlordane	Small plot study, organics were immobilized	11
Beaverton, OR	Municipal landfill cap with hybrid poplars	Organics, metals, BOD	Landfill cap successful, full scale	12
Slovenia	Landfill cap, closure with hybrid poplars	Organics, metals, BOD	Two years of growth	13
Iowa City, IA	Landfill leachate abatement with poplars	Chlorinated solvents, metals, BOD, NH3	Poplars survived in lab, 1200 mg/L	14
Prince George's County, MD	Sewage sludge in trenches, poplars on degraded lands	Nitrogen in sludge	70 tons/acre of sludge treated, full scale, 6-year plantation	15
Corvallis, OR	Organics in hydroponic system with poplars, Russian olive, soybean, green ash	Nitrobenzene and others	Essentially complete uptake in the lab	16
New Mexico	Contaminated soil with Datura sp. and Lycoper sconsium	Trinitrotoluene (TNT)	Essentially complete treatment	17
Oak Ridge, TN	Organics-contaminated soils with millet, goldenrod, Bahiagrass	Trichloroethylene and others	Enhanced biomineralization	5
Salt Lake City, UT	Contaminated soil by crested wheatgrass	Pentachlorophenol and phenanthrene	Enhanced soil mineralization	18
New Jersey, Illinois	Shallow groundwater and poplars	NO3, NH3	Decreased size of plume	19
McMinnville, OR	Landfill leachate irrigation on 4 acres of poplars	NH3, salts	Zero discharge, alternative to pumping to wastewater treatment plant	20
Childersburg, AL	Soil with organic matter	TNT	Enhanced degradation, pilot scale	

is keeping the site natural and free from infiltration. Now in its third year, the project of evapotranspiration by the trees has kept the landfill free from leachate problems. Nearby residents accept the innovative solution, preferring the forest to a barren plastic or clay cap. A full-scale application (14 acres, 40,000 trees) using drip irrigation of landfill leachate on poplar trees has also proven effective at a McMinnville, OR, site. Although hybrid poplars seem to tolerate organic chemicals quite well, high concentrations of metals, salts, and ammonia are toxic.

Table 2 includes some recent applications of phytoremediation. Some are pilot or greenhouse studies, but most are full-scale operations. They span a range of pollutants from atrazine to TNT and several different plant species.

Limitations of phytoremediation

Researchers studying phytoremediation face some potential limitations. They still need to establish whether contaminants can collect in leaves and be released during litter fall or accumulate in fuelwood or mulch. It may be difficult to establish the vegetation because of soil toxicity or possible migration of contaminants off site by binding with soluble plant exudates. Possible migration of contaminants off site by binding with soluble plant exudates is a concern, but to date none of these problems has been observed. In some situations, regulatory restrictions will not allow contaminants to be left in place, even when a vegetative cover prevents erosional pathways of exposure.

Phytoremediation is most effective at sites with shallow contaminated soils, where nutrient and organic contaminants can be treated in the rhizosphere and by root uptake. Although deep-contaminated sites and those with deep pools of nonaqueous-phase liquids are not good applications, deep groundwater contaminants or leachate pond effluent may be treated by pumping and drip irrigation on plantations of trees.

Degradation of organics in conjunction with plant enzymes is so fast that desorption and mass transport of chemicals from the soil may become the rate-determining step. Therefore, phytoremediation may require more time to achieve cleanup standards than alternatives such as excavation or ex situ treatment, especially for hydrophobic pollutants that are tightly bound to soil particles.

EPA has not adopted phytoremediation as an approved technology, although we have been given special permission by the states to use hybrid poplar

Photo 3. Phytoremediation at a landfill: (above) Landfill slope in Beaverton, OR, before trees were planted; (below) Same site only one year after hybrid poplar trees were planted in 4 ft of soil as a cap and closure at the landfill. Trees keep the landfill dry by evapotranspiration. A dense, deep root system is shown by excavation of the roots to 6 ft.

trees as caps at several landfills as an alternative to a Subtitle D cap under the Resource, Conservation, and Recovery Act. However, the technology is still not widely used.

A comparison of costs with those for the standard practices of soil venting, soil washing, excavation, or bioremediation is not possible because phytoremediation is too new. Our experience indicates that it should be very competitive with other technologies. Planting costs are ~ $10,000 per acre, and monitoring costs would be similar to those for other alternatives. In many cases, we view phytoremediation as a final "polishing step" to close sites after other cleanup technologies have been used to treat the hot spots.

Although phytoremediation is not a panacea for hazardous waste problems, it has proven effective in several applications for treatment of shallow contaminated sites. Before the technology can mature, we need a better understanding of the role of metabolites, enzymes, and the selection of plant systems for various wastes. Nevertheless, the technology holds great promise. In general, plants can withstand greater concentrations of organic pollutants than most microorganisms; they can take up the chemicals quickly and convert them to less toxic me-

tabolites, and they are known to stimulate degradation of organics in the rhizosphere.

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MEMORANDUM

TO: Gary Cipriano, Chicago

FROM: Shawn Sager, Raleigh

DATE: May 16, 1996

RE: **UNO-VEN Risk Assessment**

The following summarizes the screening risk assessment prepared using the Illinois Tiered Approach to Cleanup Objectives (TACO) Guidance document (Illinois Environmental Protection Agency [IEPA]) The focus of the risk assessment is the former land treatment facility at the UNO-VEN Refinery in Lemont, Illinois. Volunteer vegetation currently covers the site. Geraghty & Miller proposes closure of the former land treatment facility using poplar trees and grasses as a vegetative cover. The treatment zone soils will not be covered by any fill or topsoil. The purpose of this risk assessment is to aid in the development of this remedial option for the site.

The risk assessment is divided into the following sections:

- **Constituent Characterization:** summarizes the data collected at the site, compares the soil data to the Illinois Tier 1 levels, and identifies the inorganics to be carried through the risk assessment (i.e., inorganics of potential concern) used to establish Tier 2 levels.

- **Toxicity Assessment:** identifies and presents toxicity values for the inorganics of potential concern.

- **Exposure Characterization:** discusses potential exposure routes, potential receptors, and intake assumptions used to develop site-specific levels.

- **Tier 2 Analysis:** presents the Tier 2 cleanup objectives and compares them to the concentrations detected at the site.

- **Ecological Risk Assessment:** presents the ecological risk assessment.

- **Uncertainties:** discusses the uncertainties in the risk assessment process.

- **Conclusions:** presents conclusions of the risk assessment.
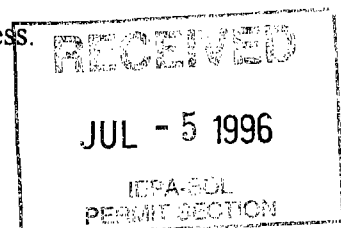
CONSTITUENT CHARACTERIZATION

This section discusses the occurrence of constituents detected in soils at the former land treatment facility at the UNO-VEN Refinery.

DATA REDUCTION

The data were reduced and analyzed for use in the risk assessment according to the guidelines provided by the U.S. Environmental Protection Agency (USEPA) (1989a, 1994a). For constituents within a data group reported as non-detected (non-detects), one-half of the sample quantitation limit (SQL) was used as a proxy concentration rather than using zero or eliminating the data point.

The results of the statistical analyses are presented in the constituent occurrence tables (Table 1). The information in these tables includes, for each detected constituent:

- the frequency of detection (ratio of the number of detects to the total number of samples in that group),

- the range of SQLs used as proxy concentrations for non-detects in the statistical calculations,

- the range of detected values,

- the arithmetic mean, and

- the 95 percent upper confidence level (UCL) on the arithmetic mean (assuming a one-tailed distribution).

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Both mean and UCL concentrations were calculated using proxy concentrations for non -detects.

The one-sided UCL is a statistical number calculated using the following formula:

$$UCL_{95} = \bar{x} + \frac{s x\, t_{0.05,n-1}}{\sqrt{n}}$$

where:

n	sample size (number of data points);
s	sample standard deviation;
$t_{0.05,n-1}$	0.05 critical value for the t_{n-1} distribution;
UCL_{95}	95 percent upper confidence level for the mean; and
$\bar{x}$	sample mean (average).

If the samples were selected randomly from the site, a 95 percent confidence level exists that the arithmetic mean concentration for the site lies below the UCL concentration. A high level of confidence (95 percent) is used to compensate for the uncertainty involved in representing the site conditions with a finite number of samples.

SOIL DATA

Twelve inorganics were detected in surface soil samples from the Land Treatment Facility at the UNO-VEN Refinery site, as seen in Table 1. Most constituents were detected in all of the samples. The exceptions were selenium which was detected in 13 of 29 samples; cadmium which was detected in 25 of 29 samples; and antimony which was detected in 27 of 29 samples.

Following the IEPA TACO guidance, maximum soil concentrations were compared with the Tier 1 levels. Groundwater in the area of the site may be used as a water supply. Toxicity characteristic leaching procedure (TCLP) data were obtained on selected samples collected in the Land Treatment Facility. As seen in Table 2, all of the constituents were detected below the TCLP acceptable level. As a result, the leaching to groundwater pathway can be removed from this analysis. Instead, the maximum soil concentrations were compared with Tier 1 screening

levels for ingestion or inhalation exposures. (The lower screening level for these two exposure pathways is presented in Table 1.)

The Tier 1 screening analysis reveals that the maximum detected concentration for antimony, barium, cadmium, cobalt, mercury, nickel, selenium, and vanadium were below the Tier 1 screening levels. As a result, these constituents were not included in the further analysis for the site. Arsenic, beryllium, chromium, and lead initially were included in the analysis.

Of the four constituents not detected below the Tier 1 screening levels, lead poses a special problem. There are no toxicity values available for lead. The Tier 1 screening level is based on a USEPA directive.

TOXICITY ASSESSMENT

Risk associated with exposure to chemical constituents is a function of the toxicity and exposure dose. In assessing human-health risks, a distinction is made between non-carcinogenic and carcinogenic effects. This section discusses these two categories of toxic effects and the toxicity values used to calculate human-health risk. For potential carcinogens, the current regulatory guidelines (USEPA, 1989a) use an extremely conservative approach in which it is assumed that any level of exposure to a carcinogen hypothetically could cause cancer. This is contrary to the traditional toxicological approach, which still is applied to non-carcinogenic chemicals where finite thresholds are identified, below which toxic effects have not occurred.

NON-CARCINOGENIC EFFECTS

For many non-carcinogenic effects, protective mechanisms must be overcome before the effect is manifested. Therefore, a finite dose (threshold), below which adverse effects will not occur, is believed to exist for non-carcinogens. A single compound might elicit several adverse effects depending on the dose, the exposure route, and the duration of exposure. Chemicals may exhibit their toxic effects at the point of application or contact (local effect), or they may exhibit

systemic effects after they have been distributed throughout the body. Most chemicals that produce systemic toxicity do not cause similar degrees of toxicity in all organs, rather they exhibit the major toxicity on one or two target organs.

For a given chemical, the dose or concentration that elicits no effect when evaluating the most sensitive response (the adverse effect which occurs at the lowest dose) in the most sensitive species is referred to as the no observed effect level (NOEL). The NOEL is used to establish toxicity values (called reference doses [RfDs] for oral exposures and reference concentrations [RfCs] for inhalation exposure). The RfD and RfC are estimates of a daily exposure level that is unlikely to cause non-carcinogenic health effects. Therefore, exposure levels must exceed a threshold dose to produce toxic effects. Chronic RfDs and RfCs are used to assess long-term exposures ranging from 7 years to a lifetime. Subchronic RfDs and RfCs are used to evaluate the potential for adverse health effects associated with exposure to chemicals during a period of a few days to 7 years. Subchronic RfDs are used to evaluate potential excavation worker exposure.

While the RfD is an estimated dose of a chemical that will not cause adverse health effects, the RfC is an estimated concentration in air that will not cause adverse health effects. The RfC accounts for the dynamics of the respiratory system, diversity between species, and the difference in physicochemical properties of chemical constituents. Therefore, parameters such as deposition, clearance mechanisms, and the physicochemical properties of the inhaled agent are considered in the determination of the effective dose delivered to the target organ. RfD and RfC values used in this risk assessment were obtained from Integrated Risk Information System (IRIS) (1995) and Health Effects Assessment and Summary Tables (HEAST) (USEPA, 1995). Table 3 summarizes the RfDs and RfCs for the constituents of interest.

CARCINOGENIC EFFECTS

The induction of cancer in humans and in animals by chemicals proceeds through a complex series of reactions and processes. As with non-carcinogenic effects, chemicals may exhibit their toxic effects at the point of application or contact (local effect), or they may exhibit

systemic effects after they have been distributed throughout the body. In the case of carcinogens, the target organ is the site of tumor formation.

Chemical constituents are classified as known, probable, or possible human carcinogens based on a USEPA weight-of-evidence scheme in which chemicals are systematically evaluated for their ability to cause cancer in humans or laboratory animals. The USEPA classification scheme (USEPA, 1989a) contains five classes based on the weight of available evidence, as follows:

A	Known human carcinogen;
B	Probable human carcinogen;
	B1 Probable human carcinogen -- limited evidence in humans;
	B2 Probable human carcinogen -- sufficient evidence in animals and inadequate data in humans;
C	Possible human carcinogen -- limited evidence in animals;
D	Inadequate evidence to classify; and,
E	Evidence of non-carcinogenicity.

Constituents in Classes A, B1, B2, and C generally are included in risk assessments as potential human carcinogens; however, Class C carcinogens may be evaluated on a case-by-case basis (USEPA, 1989a). There are four carcinogenic constituents of concern. Arsenic and chromium VI (through the inhalation route only) are Class A carcinogens, and beryllium and lead are a Class B2 carcinogens. Chromium III is not classified as a carcinogen.

Currently, the USEPA uses the linearized multistage model for extrapolating cancer risk from high doses associated with occupational exposure or laboratory animal studies to low doses typically associated with environmental exposures. The model provides a 95 percent upperbound estimate of cancer incidence at a given dose. The slope of the extrapolated curve, called the cancer slope factor (CSF), is used to calculate the probability of cancer associated with an ingested dose. Inhalation exposures are evaluated using the inhalation unit risk factor (UR_i). The

unit risk is the expected excess cancer risk resulting from continuous, lifetime exposure to air containing 1 microgram per cubic meter ($\mu g/m^3$) of the chemical constituent. CSFs and UR_is used in this risk assessment are taken from IRIS (1995) or HEAST (USEPA, 1995). CSFs and UR_is are derived from the assumption that any dose level has a probability of causing cancer. The cumulative dose, regardless of the exposure period, determines the risk; therefore, separate CSFs and UR_is are not derived for subchronic and chronic exposure periods. Table 4 presents the CSFs and Ur_is.

EXPOSURE ASSESSMENT

This section addresses the potential for human and ecological exposure to constituents detected in surface soil. This section identifies the potential receptors, exposure points, exposure routes, and complete exposure pathways considered in the risk assessment. Subsequent sections of this risk assessment combine the results of the exposure assessment with constituent-specific toxicity information to characterize potential risks.

Exposure can occur only when the potential exists for a receptor to directly contact released constituents or when mechanism exists for the released constituents to be transported to a receptor. Without exposure, there is no risk; therefore, the exposure assessment is one of the key elements of a risk assessment. An exposure pathway is defined by four elements: (1) a source and mechanism of constituent release to the environment; (2) an environmental transport medium for the released constituent; (3) a point of potential contact with the contaminated medium (the exposure point); and (4) an exposure route at the exposure point. The objective of the exposure assessment is to estimate the types and magnitudes of exposure to the constituents of concern, known through sampling to occur in soil, that are present at the site.

Exposure Point Concentrations (EPCs) are the lesser of the maximum detected concentration and the 95 percent UCL on the arithmetic average calculated using proxy concentrations for non-detects. EPCs are assumed to remain constant over the expected exposure period; however, environmental fate and transport data may be used to provide a more

thorough evaluation of conservativeness of this assumption. The EPCs are compared with the Tier 2 Cleanup Objectives in the next section of the risk assessment to determine if there is a potential threat to human health.

The land treatment facility, consisting of four landfarm plots, is no longer in use. The four landfarm plots are covered with volunteer vegetation. Site workers travel by motor vehicle to the decant pond a daily basis. To be conservative, it was assumed that future site workers contact the soils near the landfarm plots. The other exposure pathway that can be envisioned is one involving construction workers who could contact the inorganics present in soil during initial installation of trees or groundcover relative to the proposed vegetative remedy. In each case, these workers were assumed to incidentally ingest the soil and inhale particulates. In the construction worker exposure scenario it is conservatively assumed that the soils are bare and do not have the protective vegetative layer.

Current risk assessment guidance requires that the averaging period used to calculate average daily exposure doses depends on the toxic effect (cancer or non-cancer). For cancer effects, the total cumulative dose was averaged over a lifetime (70 years), whereas the total cumulative dose was averaged over the exposure period for non-cancer effects. The approach for carcinogens is based on the assumption that any dose may induce a response (non-threshold) and a given dose has the same probability of inducing a response regardless of the exposure period. In other words, a higher dose received over a short exposure period is equivalent to a lower dose received over a lifetime, as long as the total dose is the same.

The exposure assumptions used in this analysis were derived from the IEPA TACO guidance, or if not available from that source, the USEPA Superfund guidance documents. One deviation from the TACO Tier 2 guidance was the use of site-specific exposure information for the site maintenance worker. They are presented for a site maintenance worker and a hypothetical future excavation worker.

SITE MAINTENANCE WORKER

The exposure assumptions used to evaluate exposure of a site maintenance worker to soil in the former land treatment area, assumes there is no vegetative cover and that the workers use the area, even though, currently, this does not occur.

(1)   Body weight of 70 kilograms (kg),

(2)   Exposure frequency of 12 days per year,

(3)   Exposure period of 25 years,

(4)   Exposure time of 8 hours per day,

(5)   Ingestion rate of 50 milligrams per day (mg/day),

(6)   Averaging period of 70 years for carcinogenic effects and 25 years for non-carcinogenic effects.

CONSTRUCTION WORKER

Currently, there is no direct exposure to constituents in the treatment zone soils. However, the potential exists for construction workers to be exposed to constituents in surface and subsurface soil at the site during future efforts to plant trees or groundcover relative to the proposed vegetative cover. Construction workers could be exposed to soil through incidental ingestion and inhalation of fugitive dust. Construction and contracting firms report that the time required to install building footings or build a foundation varies depending on the size of the building and other site-specific factors. Excavation activities associated with installing underground cables or piping would require less time than installing a building foundation. An exposure duration of 9 weeks was identified in the IEPA TACO guidance, and this is expected to be a reasonable exposure duration for a hypothetical future construction worker at the site. The exposure assumptions for the hypothetical future construction worker exposed to soil are listed below.

(1)   Body weight of 70 kg,

(2)   Exposure frequency of 5 days per week,

(3)   Exposure period of 9 weeks,

(4)   Exposure time of 8 hours per day,

(5)   Ingestion rate of 480 mg/day, and

(6)   Averaging period of 70 years for carcinogenic effects and 9 weeks for non-carcinogenic effects.

TIER 2 ANALYSIS

Tier 2 Cleanup Objectives were developed for the two exposure scenarios identified in the previous section: site worker exposure to soil and hypothetical future construction worker exposure to soil. Tier 2 Cleanup Objectives are constituent concentrations considered to be protective of human health if exposure were to occur. The Tier 2 Cleanup Objectives are compared to the EPCs.

The Tier 2 Cleanup Objectives were calculated following guidance provided by the IEPA in their TACO guidance and the USEPA (1991b). This approach combines constituent-specific hazard information with conservative (i.e., health protective) assumptions about medium-specific exposure in order to derive medium-specific concentrations that will be protective of human health. In calculating Tier 2 Cleanup Objectives, the equations from the above-referenced documents were used in which potential cancer risk or non-cancer risk was set at a level that would not require remediation. Consistent with TACO and USEPA guidance, the "target" risk levels were set at a target excess lifetime cancer risk of 1×10^{-6} for each potential carcinogen and a target hazard quotient equal to one.

Evaluation of lead presents a problem in preparing risk assessments. Lead does not have a cancer slope factor or a reference dose. Instead, the relationship between exposure and the potential for adverse health effects can be evaluated by predicting blood lead levels. This approach was used to identify the Tier 1 screening level of 400 mg/kg. Additionally, USEPA

(1994b) has stated that the 400 mg/kg should be used for residential soils. Restrictive covenants will be in place to ensure the site is not available for future residential use. Therefore, the 400 mg/kg value represents a very conservative estimate of exposure. Historically, USEPA (1992b) used a range of acceptable lead concentrations of 500 mg/kg to 1,000 mg/kg. The latter concentration being considered appropriate for industrial settings. Using this comparison to 400 mg/kg, the maximum concentration of lead in soils would be considered acceptable.

Information regarding the inherent toxicity of each constituent was used in the equations, as were parameters representing conservative exposure scenarios. The exposure assumptions were outlined in the previous section. The equations were solved for the medium-specific concentration of each constituent not requiring remediation.

SITE MAINTENANCE WORKER

Although site workers are not expected to contact the soils in the former land treatment farm, potential exposure to these soils was evaluated. Exposure is expected to be much less than that described in the previous section and used here to derive the Tier 2 Cleanup Objectives. This is because the soils at the former land treatment facility are covered with volunteer vegetation which reduces the possibility for contact with the soil. Table 5 presents the equations used to derive the Tier 2 Cleanup Objectives. Table 6 presents the results. Comparing the EPCs in Table 1 to the Tier 2 Cleanup Objectives in Table 6, at a 1×10^{-6}, the EPCs for arsenic, beryllium, and chromium are less than the calculated Tier 2 Cleanup Objectives. Therefore, this exposure pathway presents no threat to human health.

CONSTRUCTION WORKERS

The former land treatment area is not used at this time, and there are no plans to redevelop the area. The calculated Tier 2 levels assume construction workers would contact treatment zone soils during implementation of the proposed vegetative remedy. The exposure assumptions were outlined in an earlier section. They were used in the equations presented in Table 5. The Tier 2

Cleanup Objectives derived for this exposure pathway are presented in Table 7. Comparing these concentrations to the EPCs presented in Table 1, it is seen that all of the EPCs are below the Tier 2 Cleanup Objectives. Therefore, there is not potential threat to human health from this pathway.

ECOLOGICAL ASSESSMENT

The objective of the ecological risk assessment (ERA) is to evaluate existing metals data for treatment zone soils and plant tissue collected at the site to determine potential site-related ecological effects. The standard paradigm for predictive ERA, as presented in the USEPA Framework for Ecological Risk Assessment (USEPA, 1992a) and the Ecological Risk Assessment Guidance for Superfund (USEPA, 1994b), was adapted to the ecological assessment of the site. Other technical guidance used included Risk Assessment Guidance for Superfund - Volume II, Environmental Evaluation Manual (USEPA, 1989b) and Ecological Assessment of Hazardous Waste Sites: A Field and Laboratory Reference (USEPA, 1989c).

A phased approach was implemented to determine potential ecological risks associated with the site. The goal of the phased approach was to use resources efficiently by performing tasks as is necessary to provide sufficient data for making decisions. At each phase, the decision was made whether to proceed and how best to proceed, based on the data collected up to that point.

Phase I of the ecological risk assessment involved the compilation and review of available environmental quality information (i.e., results of previous and ongoing soil investigations) and comparing this information with available criteria, standards and/or benchmark values to preliminarily determine potential ecological risks. Currently, there are no established state or federal soil standards or criteria for the protection of ecological receptors. Therefore, comparison benchmark values for the protection of terrestrial vegetation were derived based on the lowest concentration reported to be toxic to plants.

The phytotoxicity information for the toxicity of metals to terrestrial plants was obtained from searches of bibliographic and numeric databases (BIOSIS, PHYTOTOX), review articles, and

conventional literature searches. Soil benchmarks are based on data provided by toxicity studies in either the field, greenhouse, or laboratory settings.

A comparison of constituent concentrations detected in soil with soil phytotoxicity benchmark values is presented in Table 8. Concentrations of arsenic, chromium, lead, mercury, and nickel exceeded available phytotoxicity values for soil.

Plant tissue (grasses and poplar leaves) was collected at the site and analyzed for arsenic, cadmium, chromium, and lead. For those constituents for which data was not available, constituent concentrations in vegetation were estimated using soil to plant uptake factors obtained from Baes et al. (1984). A comparison of constituent concentrations detected in plant tissue with plant tissue phytotoxicity benchmark values is presented in Table 9. Plant tissue phytotoxicity benchmark values were not exceeded by constituent concentrations detected in, or modeled for, plant tissue at the site. Additionally, the concentrations of several constituents detected in vegetation collected at the site were less than those detected in background samples (Table 9).

The derived benchmarks serve for preliminary constituent screening. Plant toxicity may be affected by many factors such as soil characteristics (pH, moisture, organic matter, clay content, redox potential, etc.), plant sensitivity, input-output balance, and cumulative effects. Therefore, if constituent concentrations reported in soils at the site support vigorous and diverse plant communities, or if a benchmark is less than background soil concentrations, it is reasonable to conclude that potential risk at the site is limited. As previously indicated, the site has been inactive since 1989 and supports growth of volunteer and pioneer species. Therefore, soils at the site currently support and promote vegetative cover and do not appear to have toxic effects.

Phase II of the ecological risk assessment involved the comparison of estimated daily constituent doses with toxicological benchmarks to determine potential to wildlife that may use the site. This comparison, called the hazard quotient (HQ) method, compares estimated expected environmental concentrations (EEC) for a specific constituent or daily doses to benchmark values to determine whether the EEC or receptor dose is less than or equal to an acceptable or "safe" dose. The

HQ is defined as the ratio of the estimated daily dose of a constituent through a particular exposure route to the benchmark for the same constituent through that ingestion route. This process is similar to the calculation of the HQ for human health. The comparison will be made for each constituent and is expressed as:

$$HQ = Dose\ (mg/kg\text{-}day)/benchmark\ (mg/kg\text{-}day)$$

where:

HQ	=	Hazard quotient;
Dose	=	Estimated constituent dose for a given receptor; and
benchmark	=	Toxicological benchmark value.

Using this method, the degree to which a particular constituent concentration exceeds a toxicological benchmark can be evaluated. Therefore, an HQ greater than 1 indicates that a given exposure dose exceeds the toxicological benchmark for a particular species. The greater the HQ, the greater the exceedence. An HQ less than 1 indicates that, for a particular constituent-species interaction, ecological risks are unlikely to occur.

The endpoint assessed for the site was effects on herbivorous wildlife populations sufficient to impair reproduction. The Eastern cottontail rabbit (*Sylvilagus floridanus*) was selected as an indicator species to evaluate this endpoint because it is societal, has a range small enough to be associated with the site, and is widespread such that it is likely to occur on the site. Constituent concentrations in food sources (e.g., an average daily dose) were calculated for the rabbit and compared to toxicological benchmark values as a measurement of this endpoint.

Potential exposure pathways for the rabbit at the UNO-VEN site include ingestion of food (grasses, foliage) and incidental ingestion of surface soil. The daily dose of constituents for the rabbit was estimated by the following equation:

$$I \quad = \quad \frac{[(Cveg)^*(Iveg) + (Cs)^*(Is)\}^*(H)]}{BW}$$

where:

I = Total estimated constituent intake (mg/kg/day);

Cveg	=	Constituent concentration in vegetation (mg/kg);
Iveg	=	Ingestion rate of vegetation (kg/day);
Cs	=	Constituent concentration in soil (mg/kg);
Is	=	Ingestion rate of soil (kg/day);
H	=	Area use factor (home range/area of concern) (unitless); and
BW	=	Body weight (kg).

Information required to estimate constituent exposure for the rabbit was obtained from the available literature. The food consumption rate is reported to be 0.068 kg/day (USEPA, 1993) and the incidental soil ingestion rate is reportedly 6.3 percent of the food ingestion rate, or 0.0043 kg/day (USEPA, 1983). The average cottontail rabbit body weight is 0.7 kg (USEPA, 1993) and the home range is approximately 2 acres (USEPA, 1993). The area of concern at the site is approximately 13.5 acres.

Estimates of exposure to constituents by wildlife species were calculated using the 95 percent UCL constituent concentration detected in soil. Because wildlife species are mobile, likely use various portions of the site, and can be exposed through multiple media pathways, the 95 percent UCL best represents the spatial integration of constituent concentrations to which wildlife species would be exposed.

Data on the constituent concentration in vegetation (Cveg) was available for arsenic, cadmium, chromium, and lead. Where constituent concentrations were not available, constituent concentrations in vegetation were estimated using soil-to-plant uptake factors (PU) obtained from Baes et al. (1984). Soil-to-plant uptake factors estimate constituent concentrations on a dry weight basis. Therefore, a dry-to-wet conversion factor must be used to represent fresh vegetation. Based on the assumption that fresh foliage is 85 percent water (USEPA, 1993), constituent concentrations in fresh vegetation is estimated by the following equation:

$$\text{Foliage}_{\text{fresh}} = \text{Foliage}_{\text{dry}} * (1-W)$$

where:

Foliage$_{\text{fresh}}$	=	Constituent concentration in fresh vegetation (mg/kg);
Foliage$_{\text{dry}}$	=	Constituent concentration in dry vegetation (mg/kg); and
W	=	proportion of water in vegetation (0.85) (unitless).

Therefore, Cveg is calculated by multiplying the constituent concentration in soil by the PU and by 1-W.

Toxicity information derived from the literature was used to develop benchmark values for the rabbit. By comparing constituent concentrations measured at the UNO-VEN site to these benchmarks, the likelihood that constituents pose a risk to ecological receptors was determined. Calculated exposure doses and constituent concentrations were compared to benchmarks to derive hazard quotients (HQs) used in the assessment. To determine potential hazards to the rabbit, benchmarks related to reproductive endpoints were used whenever possible. Reproductive endpoints generally are considered protective at the population level, against sublethal adverse effects associated with chronic exposure to a particular constituent. However, based on a comprehensive review of the scientific literature, measurement endpoints related to reproductive effects were not available for some constituents.

The chronic NOAELs presented are based on experimental studies on laboratory animals. When necessary, the authors (Opresko et al., 1993) used uncertainty factors of 10 when extrapolating from acute or subchronic studies to chronic effects and when extrapolating from lowest-observed-adverse-effects levels (LOAELs) to NOAELs (Opresko et al., 1993).

The chronic NOAELs for the test species were adjusted further using a scaling factor to account for differences in body weights between the test species and the indicator species. Larger animals have lower metabolic rates and therefore have lower rates of detoxification than smaller animals (Opresko et al., 1993). The following equation from Opresko et al. (1993) was used to account for body weight differences for each constituent:

$$\text{chronic NOAEL}_i = \text{chronic NOAEL}_t \times (BW_t/BW_i)^{1/3}$$

where:

chronic NOAEL$_i$	=	chronic NOAEL for indicator species;
chronic NOAEL$_t$	=	chronic NOAEL for test species;
BW$_i$	=	body weight of indicator species; and

$$BW_t \qquad = \qquad \text{body weight of test species.}$$

The body weights of the test species and the were taken from Opresko et al. (1993) Toxicological benchmarks for the rabbit are presented in Table 10.

Potential risks to herbivorous wildlife were assessed by comparing estimated daily doses of constituents detected in surface soil at the UNO-VEN site with toxicological benchmark values using the eastern cottontail rabbit as an indicator species. The rabbit was assumed to be exposed to constituents through ingestion of constituents in vegetation and the incidental ingestion of constituents in soil. Hazard quotients (HQs) and the cumulative hazard index (HI) for the rabbit are presented in Table 11. The cumulative HI is 1. No constituent produced an HQ greater than 1 for the rabbit. Therefore, constituent concentrations detected in soil and grasses at the UNO-VEN site are unlikely to present a risk to herbivorous receptors.

UNCERTAINTIES

The Tier 2 Cleanup Objective levels presented here for the former land treatment facility at the UNO-VEN Refinery are conservative estimates of soil concentrations which would not cause adverse non-cancer health effects or potential excess lifetime cancer risks at the 1×10^{-6} (1 in a million) level. If the exposure scenarios were to occur, actual risks experienced by the potentially exposed population would be almost certainly lower than those generally considered to be unacceptable by the State of Illinois and the USEPA. It is important to realize that considerable uncertainty is inherent in the risk assessment process. Sources of uncertainty include monitoring data, exposure models, and values of the variables used to calculate intakes.

Uncertainty always exists in using a finite set of monitoring data to represent site conditions. Initially, to be conservative, the maximum concentrations were compared to the Tier 1 levels. To be a little more realistic, but to account for this uncertainty, the calculated Tier 2 Cleanup Objectives were compared to the UCL concentrations.

Exposure scenarios contribute uncertainty to the risk assessment. Tier 2 Cleanup Objectives were calculated based on the assumption that the current conditions with respect to constituent concentrations would remain constant throughout the exposure period. If the source were eliminated or present below the ground surface, the risks from potential exposures would be reduced.

The toxicity values and other toxicological (health effects) information used in this report are associated with significant uncertainty. Most health effects information was developed using laboratory animals exposed to high doses. Although species differences in absorption, distribution, metabolism, excretion, and target organ sensitivity are well documented, available data are not sufficient to allow compensation for these differences. Most laboratory studies strictly control as many factors as possible, yet the human population is genetically diverse and affected by a variety of dietary, occupational, pharmaceutical, and other factors. When human epidemiological data are available, a different set of uncertainties is present. For instance, exposure dose is seldom well characterized in epidemiological studies.

CONCLUSIONS

This risk assessment was prepared to evaluate whether inorganic constituents in soils at the former land treatment facility at the UNO-VEN Refinery pose a threat to human health or the environment. The IEPA TACO guidance and other referenced guidance were used to identify whether conditions at the former land treatment facility at the UNO-VEN Refinery pose a threat to human health under relevant exposure conditions. Because TCLP data were below regulatory limits, the potential for leaching to groundwater was not considered in the Tier 1 assessment. Initially, maximum concentrations of inorganic constituents detected in soils were compared with Tier 1 levels presented in the IEPA TACO guidance. Comparison to Tier 1 levels was necessary only for the ingestion and inhalation pathways. Antimony, barium, cadmium, cobalt, mercury, nickel, selenium, and vanadium were excluded from further evaluation based on this comparison. Arsenic, beryllium, chromium, and lead were carried through the remainder of the risk assessment.

Two potential exposure scenarios were used to establish Tier 2 levels: exposure of site workers to soil and exposure of construction workers to soil. Comparing the EPCs to the Tier 2 Cleanup Objectives derived for both these scenarios revealed the following. For both exposure scenarios, all of the EPCs were less than the calculated Tier 2 Cleanup Objectives. Therefore, no threat to human health is indicated under the assumed exposure conditions.

An ecological risk assessment was completed to evaluate existing metals data for treatment zone soils and plant tissue collected at the site to determine potential site-related ecological effects. A comparison of constituent concentrations measured in soil, and measured and modeled in plant tissue, with available benchmark values indicates that phytotoxicity risks associated with constituent levels detected in soils at the site would not be expected. Potential risks to herbivorous wildlife were assessed by comparing estimated daily doses of constituents detected in surface soil at the UNO-VEN site with toxicological benchmark values using the eastern cottontail rabbit as an indicator species. Metals concentrations detected in soil and grasses at the UNO-VEN site are unlikely to present a risk to herbivorous receptors since no metal resulted in an HQ greater than 1 for the rabbit and the cumulative HI for metals is 1.

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Table 1.   Occurrence Summary for Surface Soil Samples, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Constituent	Frequency Detects / Total	Range of SQLs Min - Max	Range of Detects Min - Max	Mean	UCL	EPC	Tier 1 Screen Ingestion (a)
Inorganics							
Antimony	27 / 29	0.12 - 0.12	0.2 - 1.4	0.49	0.6	0.6	31
Arsenic	29 / 29	1E+10 1E-10	2.4 - 120	28	40	40	0.4
Barium	29 / 29	1E+10 1E-10	31 - 260	94	110	110	5,500
Beryllium	29 / 29	1E+10 1E-10	0.24 - 0.85	0.42	0.47	0.47	0.1
Cadmium	25 / 29	0.12 - 0.12	0.25 - 5.3	1.3	1.7	1.7	39
Chromium	29 / 29	1E+10 1E-10	9.2 - 1,400	470	600	600	140 (b)
Cobalt	29 / 29	1E+10 1E-10	6.1 - 21	10	11	11	4,700
Lead	29 / 29	1E+10 1E-10	12 - 480	100	140	140	400
Mercury	29 / 29	1E+10 1E-10	0.02 - 0.75	0.26	0.32	0.32	7 (b)
Nickel	29 / 29	1E+10 1E-10	17 - 110	38	44	44	1,600
Selenium	13 / 29	4E-05 - 0.00004	0.00008 - 0.016	0.0017	0.0031	0.0031	390
Vanadium	29 / 29	1E+07 1E-13	0.01 - 0.45	0.096	0.13	0.13	550

Concentrations and Tier 1 screening values are reported in milligrams per kilogram (mg/kg).

(a) Tier 1 screening values for soil ingestion pathway; leaching to groundwater not of concern at this site as all of the samples passed the TCLP.
(b) Tier 1 screening value for inhalation pathway as this value was lower than that for the soil ingestion pathway.

EPC	Exposure point concentration; lesser of the UCL and the maximum detected concentration.
Mean	Arithmetic average of the total number of samples, using proxy concentrations for non-detects.
SQLs	Practical sample quantitation limits for the non-detects.
TCLP	Toxicity characteristic leaching procedure.
UCL	95 percent upper confidence limit (one-tailed) on the mean, assuming a normal distribution.

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Table 2. TCLP Metal Concentrations (mg/l) in Soil and Sediment Samples, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Samples Analyzed for TCLP Metals	Arsenic	Chromium	Lead
Treatment Area Samples			
LAI-1TZ (0-0.5)	N/A	0.019	<0.030
LAI-2TZ (0-1)	N/A	0.022	N/A
LAI-2TZ (3-5)	<0.030	N/A	N/A
LAI-3TZ (0-1)	N/A	0.026	N/A
LAI-4TZ (0-1)	N/A	0.021	N/A
LAI-5TZ (0-0.5)	N/A	0.027	N/A
LAI-6TZ (0-1)	N/A	0.026	N/A
LAI-7TZ (0-0.5)	N/A	0.027	<0.030
LAI-8TZ (0-0.5)	N/A	<0.030	N/A
LAI-9TZ (0-1)	N/A	0.64	0.22
LAI-10TZ (0-0.5)	<0.030	0.012	N/A
LAI-13TZ (0-1)	N/A	0.031	N/A
LAI-13TZ (4.5-6.5)	<0.030	N/A	N/A
LAII-1TZ (0-1)	N/A	0.0074	N/A
LAII-3TZ (0-1)	N/A	0.0098	N/A
LAII-4TZ (0-1)	N/A	0.011	<0.030
LAII-5TZ (0-1)	N/A	0.011	N/A
LAII-6TZ (0-0.5)	<0.030	N/A	N/A
LAII-6TZ (2.5-4.5)	N/A	<0.030	N/A
LAIII-1TZ (0-0.5)	N/A	0.011	0.091
LAIII-3TZ (0-0.5)	N/A	0.024	N/A
LAIV-1TZ (0-1)	N/A	0.066	0.055
LAIV-3TZ (0-1)	N/A	0.016	<0.030
LAIV-3TZ (4.5-6.5)	N/A	0.031	N/A
LAIV-4TZ (0-1)	N/A	0.017	<0.030
LAIV-5TZ (0-1)	N/A	0.032	N/A
Regulatory Limit	5	5	5

mg/L Milligrams Per Liter
N/A Not Analyzed

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Table 2. TCLP Metal Concentrations (mg/l) in Soil and Sediment Samples,
Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Samples Analyzed for TCLP Metals	Arsenic	Chromium	Lead
Perimeter Samples			
LAI-1PS (0-1)	N/A	0.023	N/A
LAI-4PS (0-1)	N/A	0.017	N/A
LAI-11PS (0-1)	N/A	0.014	N/A
LAI-12PS (0-1)	N/A	0.29	N/A
LAI-15PS (0-1)	N/A	0.016	N/A
LAII-1PS (0-1)	N/A	<0.004	N/A
LAII-4PS (0-1)	N/A	0.020	<0.03
LAII-5PS (0-1)	N/A	0.021	N/A
LAII-10PS (0-1)	N/A	0.027	N/A
LAII-11PS (0-1)	N/A	0.027	N/A
LAII-15PS (0-1)	N/A	0.022	<0.03
LAIII-1PS (0-1)	N/A	<0.004	<0.03
LAIII-3PS (0-1)	N/A	0.0056	<0.03
LAIV-3PS (0-1)	N/A	0.0087	<0.03
Stream Sediment Samples			
SS-2 (0-1)	N/A	0.0099	N/A
Regulatory Limit	5	5	5

mg/L   Milligrams Per Liter
N/A   Not Analyzed

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Table 3.   Oral Reference Doses, Inhalation Reference Concentrations, Target Sites, and Confidence Levels for Constituents of Concern, Land Treatment Facility,
           UNO-VEN Refinery, Lemont, Illinois.

| Constituent | RfDo (mg/kg/day) | | RfC (mg/m³) | | Target Sites | | Confidence Level/ |
	Subchronic	Chronic	Subchronic	Chronic	Oral	Inhalation	Uncertainty Factor
Inorganics							
Arsenic	3.0E-04	3.0E-04	NA	NA	skin	NA	medium/3
Beryllium	5.0E-03	5.0E-03	NA	NA	none	NA	low/100
Chromium III	1.0E+00	1.0E+00	NA	NA	liver	NA	low/100
Chromium VI	2.0E-02	5.0E-03	NA	NA	NR	NA	low/500
Lead	NA	NA	NA	NA	CNS	CNS	NA

References: IRIS, 1995; USEPA, 1995.

CNS	Central nervous system.
mg/kg/day	Milligrams per kilogram per day.
mg/m³	Milligrams per cubic meter.
NA	Not available.
NR	None reported.
RfC	Inhalation reference concentration.
RfDo	Oral reference dose.

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Table 4.   Oral Cancer Slope Factors, Inhalation Unit Risks, Tumor Sites, and USEPA Cancer Classifications for Constituents of Concern,
Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Constituent	Oral CSF (kg-day/mg)	Inhalation Unit Risk (m³/μg)	Tumor site		USEPA Classification
			Oral	Inhalation	
Inorganics					
Arsenic	1.5E+00	4.3E-03	skin	respiratory tract	A
Beryllium	4.3E+00	2.4E-03	total tumors	lung	B2
Chromium VI	NAP	1.2E-02	NA	lung	A
Lead	NA	NA	NA	NA	B2

References: IRIS, 1995; USEPA,1995.

CSF   Cancer slope factor.
kg-day/mg   Kilograms-day per milligram.
m³/μg   Cubic meters per microgram.
NA   Not available.
NAP   Not applicable, since it is carcinogenic by inhalation.

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Table 5. Soil Tier 2 Cleanup Objective Equations for Exposure to Soil, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

ROUTE-SPECIFIC TIER 2 CLEANUP OBJECTIVES:

Oral:

$$(T2CO_o)_{C \, or \, NC} = \frac{(TCR \text{ or } THQ) \times BW \times (AP_C \text{ or } AP_{NC}) \times (10^6 \, mg/kg)}{IR \times EF \times EP \times [CSF_o \text{ or } (1/RfD_o)]}$$

Inhalation:

$$(T2CO_i)_{C \, OR \, NC} = \frac{(TCR \text{ or } THI) \times (AP_C \text{ or } AP_{NC}) \times 24 \, hrs/day}{[(1/VF)+(1/PEF)] \times ET \times EF \times EP \times [(UR_i/1000\mu g/mg) \text{ or } (1/RfC)]}$$

where:

$$PEF = Q/C \times \frac{3,600 \, sec/hr}{RPF \times (1-G) \times (Um/Ut)^3 \times F_X}$$

$$Q/C = \left(exp\left\{ \left[(0.1004 \times ln[A]) - 5.3466 \right] + (2.92 \times sY) \right\} \right)^{-1}$$

$$sY = 0.02685 \times \left(0.25 + \frac{[ln(A) - 11.0509]^2}{26.3608} \right)$$

CANCER EFFECTS TIER 2 CLEANUP OBJECTIVES:

$$T2CO_C = \frac{1}{\dfrac{1}{(T2CO_o)_C} + \dfrac{1}{(T2CO_i)_C}}$$

NON-CANCER EFFECTS TIER 2 CLEANUP OBJECTIVES:

$$T2CO_{NC} = \frac{1}{\dfrac{1}{(T2CO_o)_{NC}} + \dfrac{1}{(T2CO_i)_{NC}}}$$

Final Tier 2 Cleanup Objectives:

T2CO = Minimum result of $T2CO_C$ and $T2CO_{NC}$.

where:

A   Contiguous area of contamination ($54.600 m^2$.

AP_C Averaging period for cancer effects (25,550 days).

AP_{NC} Averaging period for non-cancer effects (days); EP × days/week for a construction worker; EP × 365 days/year for a site worker.

BW   Body weight (70 kg).

CSF   Cancer slope factor for oral (CSF_o) exposure (kg-day/mg; inverse of mg/kg/day) .

EF   Exposure frequency (5 days/week for a construction worker, 250 days/year for a site worker).

Table 5.   Soil Tier 2 Cleanup Objective Equations for Exposure to Soil, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

ET	Exposure time (8 hours/day).
EP	Exposure period (9 weeks for a construction worker, 25 years for a site worker).
F_X	Function of Ut/Um (unitless); $F_X = 0.18 \times [\ 8x^3 + 12x\ ] \times \exp(-x^2)$, where $x = 0.886 \times$ (Ut/Um) (USEPA 1991a).
Foc	Fraction organic carbon in soil (0.02) (USEPA, default) (USEPA, 1991a).
G	Fraction of vegetative cover (unitless); conservatively assumed as zero.
H	Henry's Law Constant (atm-m^3/mol); constituent-specific.
IR_S	Ingestion rate of soil (480 mg/day for a construction worker, 50 mg/day for a site worker).
PEF	Particulate emission factor (4.28×10^9 m^3/kg) (USEPA, default) (USEPA, 1991a).
Pt	Total soil porosity (0.35) (unitless) (USEPA, default) (USEPA, 1991a).
rs	True soil or particle density (2.65 g/cm^3) (USEPA, default) (USEPA, 1991a).
Q/C	Emission flux per unit concentration (g/m^2/sec)/(kg/m^3).
RPF	Respirable particle fraction (0.036 g/m^2/hr) (USEPA, default) (USEPA, 1991a).
RfC	Reference concentration for inhalation exposure (mg/m^3).
RfD	Reference dose for oral (RfD$_o$) (exposure (mg/kg/day).
T2CO	Health-based Tier 2 Cleanup Objectives (mg/kg); minimum of the T2CO$_C$ (based on cancer effects) and the T2CO$_{NC}$ (based on non-cancer effects), which are based on the route-specific T2COs (T2CO$_o$ for the oral route and T2CO$_i$ for the inhalation route).
sY	Intermediate value for calculation of Q/C.
T	Exposure interval (7.9×10^8 sec) (USEPA, default) (USEPA 1991a).
TCR	Target cancer risk (1×10^{-6}).
THQ	Target hazard quotient (1).
Um	Wind speed (4.5 m/s) (USEPA, default) (USEPA, 1991a).
URi	Unit cancer risk for inhalation exposure (m^3/mg).
Ut	Equivalent threshold value of windspeed at 10 meters (12.8 m/sec) (USEPA, default) (USEPA 1991a).

Example Calculation: arsenic, construction worker:

$$x\ =\ 0.886 \times \left[(12.8\ m\,/\,sec)\,/\,(4.5\ m\,/\,sec)\right]\ =\ 2.52$$

$$F_X\ =\ 0.18 \times [(8 \times 2.52^3) + (12 \times 2.52)] \times \exp[-(2..52^2)]\ =\ 0.0497$$

$$sY\ =\ 0.02685 \times \left(0.25 + \frac{[\ln(2,025\,m^2) - 11.0509]^2}{26.3608}\right)\ =\ 0.0187$$

$$Q\,/\,C = \left(\exp\left\{\left[\ 0.1004 \times \ln(2,025\ m^2) - 5.3466\right] + \left(2.92 \times 0.0187\right)\right\}\right)^{-1}\ =\ 92.54\ (g/m^2/sec)(kg/m^3)$$

$$PEF\ =\ \left[92.54\ (g/m^2/sec)\,/\,(kg/m^3)\right] \times \frac{(3,600\ sec\ /hr)}{(0.036\ g\ /m^2/hr) \times (1 - 0) \times [(4.5\ m/sec)\,/\,(12.8\ m/sec)]^3 \times (0.0497)}$$

$$=\ 4.28 \times 10^9\ m^3/kg$$

Table 5.   Soil Tier 2 Cleanup Objective Equations for Exposure to Soil, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Cancer Effects T2CO:

$$(T2CO_o)_C = \frac{(10^{-6}) \times (70 \text{ kg}) \times (25{,}550 \text{ days}) \times (10^6 \text{ mg} / \text{kg})}{(480 \text{ mg} / \text{day}) \times (5 \text{ days} / \text{week}) \times (12 \text{ weeks}) \times (1.5 \text{ kg - day} / \text{mg})}$$

$$= 4.1 \times 10^1 \text{ mg} / \text{kg}$$

$$(T2CO_i)_C = \frac{10^{-5} \times 25{,}550 \text{ days} \times 24 \text{hr} / \text{day}}{\left(\dfrac{1}{4.28 \times 10^9 \ \frac{m^3}{kg}}\right) \times 8 \ \frac{hr}{day} \times 5 \ \frac{days}{week} \times 12 \text{ weeks} \times \left(\dfrac{4.3 \times 10^{-3} \ m^3 / \mu g}{0.001 \ \mu g / mg}\right)}$$

$$= 1.3 \times 10^6 \text{ mg} / \text{kg}$$

$$T2CO_C = \frac{1}{\dfrac{1}{4.1 \times 10^1 \text{ mg/kg}} + \dfrac{1}{1.3 \times 10^6 \text{ mg/kg}}}$$

$$= 39 \text{ mg/kg}$$

Non-Cancer Effects T2CO:

$$(T2CO_o)_{NC} = \frac{(1.0) \times (70 \text{ kg}) \times (84 \text{ days}) \times (10^6 \text{ mg} / \text{kg})}{(480 \text{ mg} / \text{day}) \times (5 \text{ days} / \text{week}) \times (12 \text{ weeks}) \times \left(\dfrac{1}{0.0003 \text{ mg} / \text{kg} / \text{day}}\right)}$$

$$= 6.1 \times 10^1 \text{ mg} / \text{kg}$$

$$(T2CO_i)_{NC} = \frac{(1.0) \times (84 \text{ days}) \times (24 \text{ hrs} / \text{day})}{\left(\dfrac{1}{4.28 \times 10^9 \ \frac{m^3}{kg}}\right) \times 8 \ \frac{hr}{day} \times 5 \ \frac{days}{week} \times 12 \text{ weeks} \times \left(\dfrac{1}{NA}\right)}$$

$$= NA$$

Note: RfC not available.

$$T2CO_{NC} = \frac{1}{\dfrac{1}{6.1 \times 10^1 \text{ mg/kg}} + \dfrac{1}{NA}}$$

$$= 61 \text{ mg/kg}$$

T2CO= Minimum (39 mg/kg; 61 mg/kg) = 39 mg/kg (based on potential cancer effects).

Table 6.   Health-Based Tier 2 Cleanup Objectives for Soil Based on Site Worker Exposure, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

| Constituent | CANCER EFFECTS | | | NON-CANCER EFFECTS | | | Minimum |
| | Route-Specific T2COs (mg/kg) | | Cancer | Route-Specific T2COs (mg/kg) | | Non-Cancer | T2CO |
	Oral	Inhalation	Effects T2CO	Oral	Inhalation	Effects T2COs	(mg/kg)
	T2COo	T2C0i	T2CO$_C$	T2COo	T2COi	T2CO$_{NC}$	
Inorganics							
Arsenic	7.9E+01	1.9E+05	79	1.3E+04	NA	13,000	79
Beryllium	2.8E+01	3.4E+05	28	2.1E+05	NA	210,000	28
Chromium III	NC	NC	NC	4.3E+07	NA	NR	NR
Chromium VI	NAP	6.8E+04	68,000	2.1E+05	NA	210,000	68,000
Lead	NA	NA	NA	NA	NA	NA	NA

T2C0c (cancer effects) is calculated using a target cancer risk (TCR) of 1E-06; T2C0nc (non-cancer effects) is calculated using a target hazard index (THI) of 1.

NA   Not available; insufficient toxicity data.
NAP   Not applicable; chromium VI is not carcinogenic via the ingestion route.
NC   Not a suspected carcinogen.
NR   Not reported; SSTL greater than one million parts per million.
T2C0   Health-based Tier 2 Cleanup Objectives (mg/kg); minimum of the T2CO$_C$ (based on cancer effects) and the T2CO$_{NC}$ (based on non-cance
            which are based on the route-specific T2COs (T2COo for the oral route and T2COi for the inhalation route).

Table 7. Health-Based Tier 2 Cleanup Objectives for Soil Based on Construction Worker Exposure, Land Treatment Facility, UNO-VEN Refiner Lemont, Illlinois.

| Constituent | CANCER EFFECTS | | | NON-CANCER EFFECTS | | | Minimum |
| | Route-Specific T2COs (mg/kg) | | Cancer | Route-Specific T2COs (mg/kg) | | Non-Cancer | T2C0 |
	Oral	Inhalation	Effects T2COs	Oral	Inhalation	Effects T2CO	(mg/kg)
	$T2CO_o$	$T2CO_i$	$T2CO_C$	$T2CO_o$	$T2CO_i$	$T2CO_{NC}$	
Inorganics							
Arsenic	5.5E+01	1.7E+06	55	6.1E+01	NA	61	55
Beryllium	1.9E+01	3.0E+06	19	1.0E+03	NA	1,000	19
Chromium III	NC	NC	NC	2.0E+05	NA	200,000	200,000
Chromium VI	NAP	6.1E+05	610,000	4.1E+03	NA	4,100	4,100
Lead	NA	NA	NA	NA	NA	NA	NA

T2COc (cancer effects) is calculated using a target cancer risk (TCR) of 1E-06; T2COnc (non-cancer effects) is calculated using a target hazard index (THI) of 1.

NA   Not available; insufficient toxicity data.

NAP   Not applicable; chromium VI is not carcinogenic via the ingestion route.

NC   Not a suspected carcinogen.

T2CO   Health-based Tier 2 Cleanup Objectives (mg/kg); minimum of the $T2CO_C$ (based on cancer effects) and the $T2CO_{NC}$ (based on non-cance which are based on the route-specific T2COs (T2COo for the oral route and T2COi for the inhalation route).

Table 8.   Comparison of Surface Soil Samples and Phytotoxicity Benchmark Values, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Constituent	Frequency Detects / Total	Range of SQLs Min - Max	Range of Detects Min - Max	Mean	UCL	EPC	Soil Phytotoxicity Benchmark
Inorganics							
Antimony	27 / 29	0.12	0.2 - 1.4	0.49	0.6	0.6	5 [a]
Arsenic	29 / 29	NA	2.4 - 120	28	40	40	2 [b]
Barium	29 / 29	NA	31 - 260	94	110	110	NA
Beryllium	29 / 29	NA	0.24 - 0.85	0.42	0.47	0.47	10 [b]
Cadmium	25 / 29	0.12	0.25 - 5.3	1.3	1.7	1.7	3 [b]
Chromium	29 / 29	NA	9.2 - 1400	470	600	600	75 [c]
Cobalt	29 / 29	NA	6.1 - 21	10	11	11	25 [c]
Lead	29 / 29	NA	12 - 480	100	140	140	100 [a]
Mercury	29 / 29	NA	0.02 - 0.75	0.26	0.32	0.32	0.3 [c]
Nickel	29 / 29	NA	17 - 110	38	44	44	100 [a]
Selenium	13 / 29	0.00004	0.00008 - 0.016	0.0017	0.0031	0.0031	5 [c]
Vanadium	29 / 29	NA	0.01 - 0.45	0.096	0.13	0.13	50 [a]

All concentrations are reported in milligrams per kilogram (mg/kg).

[a]   Kloke, 1979.

[b]   Groncharuk and Sidorenko, 1986.

[c]   Linzon, 1978.

EPC   Exposure point concentration; lesser of the UCL and the maximum detected concentration.

Mean   Arithmetic average of the total number of samples, using proxy concentrations for non-detects.

SQLs   Practical sample quantitation limits for the non-detects.

UCL   95 percent upper confidence limit (one-tailed) on the mean, assuming a normal distribution.

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Table 9.   Comparison of Plant Tissue Samples and Plant Tissue Phytotoxicity Benchmark Values, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Constituent	Cs [a] (mg/kg)	PU [b] (unitless)	Modeled Cveg [c] (mg/kg)	BKG Grasses Cveg [d] (mg/kg)	Area 1 Grasses Cveg [e] (mg/kg)	BKG Poplar Cveg [f] (mg/kg)	Area 1 Poplar Cveg [g] (mg/kg)	Tissue Phytotoxicity Benchmark [h] (mg/kg)
Antimony	1.4	0.2	0.28	ns	ns	ns	ns	150
Arsenic	120	0.04	4.8	ND	ND	ND	ND	5-20
Barium	260	0.15	39.0	ns	ns	ns	ns	500
Beryllium	0.85	0.01	0.009	ns	ns	ns	ns	10-50
Cadmium	5.3	0.55	2.92	0.08	ND	0.98	1.03	5-30
Chromium	1,400	0.008	11.2	2.4	2.6	1.5	1.5	5-30
Cobalt	21	0.02	0.4	ns	ns	ns	ns	15-50
Lead	480	0.045	21.60	1.7	6.7	0.6	0.4	30-300
Mercury	0.75	0.90	0.68	ns	ns	ns	ns	1-3
Nickel	110	0.06	6.6	ns	ns	ns	ns	10-100
Selenium	0.016	0.03	0.0004	ns	ns	ns	ns	5-30
Vanadium	0.45	0.01	0.003	ns	ns	ns	ns	5-10

[a]	Constituent concentration in soil (Table 2-1).
[b]	Plant uptake factor from Baes et al., (1984).
[c]	Modeled constituent concentration in vegetation equals constituent concentration in soil multiplied by the plant uptake factor (Cveg = Cs * PU).
[d]	Constituent concentration measured in grasses collected at background location.
[e]	Constituent concentration measured in grasses collected at the site.
[f]	Constituent concentration measured in poplar leaves collected at background location.
[g]	Constituent concentration measured in poplar leaves collected at the site.
[h]	Benchmark derived from Kabata-Pendias and Pendias, 1992.
Cveg	Constituent concentration in vegetation.
Cs	Constituent concentration in soil.
mg/kg	Milligrams per kilogram.
ND	Not detected.
ns	Not sampled.
PU	Plant uptake factor.

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Table 10.   Toxicological Benchmark Values for Cottontail Rabbit, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Constituent	Test Species [a]	Experimental Value [b] (mg/kg/day)		NOAEL (mg/kg/day)	Measurement Endpoint	Reference [c]	Scaling Factor	Cottontail Rabbit Toxicological Benchmark [d] (mg/kg/day)
Inorganics								
Antimony (K tartrate)	Mouse	1.25	e	0.125	Reproduction	Schroeder et al., 1968	0.35	0.04
Arsenic	Mouse	1.26	e	0.126	Reproduction	Schroeder & Mitchner, 1971	0.35	0.04
Barium (chloride)	Rat	5.06	f	5.06	Growth	Perry et al., 1983	0.79	4.02
Beryllium (sulfate)	Rat	0.66	f	0.66	Longevity	Schroeder & Mitchner, 1975	0.79	0.52
Cadmium (soluble salt)	Mouse	1.9	e	0.19	Reproduction	Schroeder & Mitchner, 1975	0.35	0.07
Chromium III	Rat	2737	f	2737	Reproduction	Ivankovic, 1975	0.79	2172.36
Chromium VI	Rat	3.28	f	3.28	Growth, food consmp	Mackenzie et al., 1958	0.79	2.60
Cobalt	NA	NA		NA	NA	NA	NA	NA
Lead (acetate)	Rat	8	f	8	Reproduction	Azar et al, 1973	0.79	6.35
Mercury (sulfide)	Mouse	13.3	f	13.3	Reproduction	Revis et al., 1989	0.35	4.65
Mercury (methyl mercury)	Rat	0.032	f	0.032	Reproduction	Verschuuren et al., 1976	0.79	0.03
Nickel (sulfate)	Rat	40	f	40	Reproduction	Ambrose et al., 1976	0.79	31.75
Selenium	Mouse	0.75	e	0.075	Reproduction	Schroeder & Mitchner, 1971	0.35	0.03
Silver	Mouse	18.1	e	1.8	Systemic	Rungby & Danscher,1984	0.35	0.63
Vanadium (sodium metavanadate)	Rat	2.1	e	0.21	Reproduction	Domingo et al., 1986	0.79	0.17

[a]	Species in which the experimental (literature derived) value was reported.
[b]	Daily dose reported in the literature to cause toxicity endpoint.
[c]	Reference where experimental value was found.
[d]	Toxicological benchmark value = Benchmark value x scaling factor. Scaling factor is discussed in text.
[e]	Chronic LOAEL
[f]	Chronic NOAEL
mg/kg/day	Milligrams per kilogram per day.
NA	Not available.
NOAEL	No observed adverse effect level.

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Table 11. Exposure of Cottontailed Rabbit to Surface Soil and Associated Hazard Quotients, Land Treatment Facility, UNO-VEN Refinery, Lemont, Illinois.

Constituent	Cs [a] (mg/kg)	PU [b] (unitless)	Cveg (mg/kg)		Iv (kg/day)	Is (kg/day)	H (unitless)	BW (kg)	Exposure (mg/kg/day)	Benchmark [c] (mg/kg/day)	Hazard Quotient (unitless)
Inorganics											
Antimony	0.6	0.20	0.018		0.068	0.0043	0.15	0.7	0.0008	0.04	2.0E-02
Arsenic	40	0.04	ND	[d]	0.068	0.0043	0.15	0.7	0.0369	0.04	9.2E-01
Barium	110	0.15	2.475		0.068	0.0043	0.15	0.7	0.137	4.02	3.4E-02
Beryllium	0.47	0.01	0.0007		0.068	0.0043	0.15	0.7	0.0004	0.52	8.5E-04
Cadmium	2	0.55	ND	[d]	0.068	0.0043	0.15	0.7	0.0016	0.07	2.2E-02
Chromium	600	0.008	2.6	[d]	0.068	0.0043	0.15	0.7	0.591	2.60	2.3E-01
Cobalt	11	0.02	0.033		0.068	0.0043	0.15	0.7	0.011	NA	NA
Lead	140.00	0.45	6.7	[d]	0.068	0.0043	0.15	0.7	0.23	6.35	3.6E-02
Mercury	0.32	0.9	0.0432		0.068	0.0043	0.15	0.7	0.0009	4.65	2.0E-04
Nickel	44	0.06	0.396		0.068	0.0043	0.15	0.7	0.0463	31.75	1.5E-03
Selenium	0.0031	0.025	0.00001		0.068	0.0043	0.15	0.7	0.000003	0.03	1.0E-04
Vanadium	0.13	0.006	0.0001		0.068	0.0043	0.15	0.7	0.0001	0.17	7.1E-04

HI	1

[a]	Constituent concentration in surface soil from Table 2-1.
[b]	Plant uptake factor discussed in text.
[c]	Toxicological benchmark from Table 10.
[d]	Constituent concentration measured in grass samples collected at the site.

BW	Body weight.
Cs	Constituent concentration in surface soil.
Cveg	Constituent concentration in vegetation (Cs x PU x 0.15).
H	Home range/area of concern (2 acres/13.5 acres = 0.15) .
HI	Hazard index (sum of the hazard quotients).
Is	Ingestion rate of soil.
Iv	Ingestion rate of vegetation.
mg/kg/day	Milligrams per kilograms per day.
NA	Not available.
ND	Not detected.
PU	Plant uptake factor.

GERAGHTY & MILLER, INC.

DEFAULT SOIL AND DESIGN DATA INPUT

Title: UNO-VEN CLOSURE PLAN

FINAL COVER SYSTEM DESIGN

LANDFARM AREA 1

Do you want the program to initialize the soil water? ___Y___

Number of layers: ___2___

Layer data:

Layer 1
(a) thickness ___36"___ inches
(b) layer type ___1___ (1 or 2)
(c) liner leakage fraction (only for layer type 4) _____ (0 to 1)
(d) soil texture number ___9___ (1 to 20)*
(e) compacted? (only for soil textures 1 to 15) ___Y___ (Yes or No)
(f) initial soil water content (not asked if program is to initialize
    the soil water or if layer type is 3 or 4) _____ vol/vol
    (must be between wilting point and porosity)

Layer 2
(a) thickness ___60"___ inches
(b) layer type ___1___ (1 to 4)
(c) liner leakage fraction (only for layer type 4) _____ (0 to 1)
(d) soil texture number ___5___ (1 to 20)*
(e) compacted? (only for soil textures 1 to 15) ___N___ (Yes or No)
(f) initial soil water content (not asked if program is to initialize
    the soil water or if layer type is 3 or 4) _____ vol/vol
    (must be between wilting point and porosity)

Layer 3
(a) thickness _____ inches
(b) layer type _____
(c) liner leakage fraction (only for layer type 4) _____ (0 to 1)
(d) soil texture number _____ (1 to 20)*
(e) compacted? (only for soil textures 1 to 15) _____ (Yes or No)
(f) initial soil water content (not asked if program is to initialize
    the soil water or if layer type is 3 or 4) _____ vol/vol
    (must be between wilting point and porosity)

Layer 4	Layer 5	Layer 6
(a) _____	(a) _____	(a) _____
(b) _____	(b) _____	(b) _____
(c) _____	(c) _____	(c) _____
(d) _____	(d) _____	(d) _____
(e) _____	(e) _____	(e) _____
(f) _____	(f) _____	(f) _____

Layer 7	Layer 8	Layer 9
(a) _____	(a) _____	(a) _____
(b) _____	(b) _____	(b) _____
(c) _____	(c) _____	(c) _____
(d) _____	(d) _____	(d) _____
(e) _____	(e) _____	(e) _____
(f) _____	(f) _____	(f) _____

Layer 10	Layer 11	Layer 12
(a) _____	(a) _____	(a) _____
(b) _____	(b) _____	(b) _____
(c) _____	(c) _____	(c) _____
(d) _____	(d) _____	(d) _____
(e) _____	(e) _____	(e) _____
(f) _____	(f) _____	(f) _____

If soil texture number of layer 1 is between 1 and 15, enter:

        Type of vegetation: __FAIR__   (1 to 5)

        SCS runoff curve number (optional): _____   (0 to 100)

If the soil texture number of layer 1 is between 16 and 20, enter:

        SCS runoff curve number: _____   (0 to 100)

If landfill is open, enter potential runoff fraction: __N__   (0 to 1)

Surface area: __239580__   square feet

Slope of top liner/drain system: _____   percent
Distance from crest to drain in top liner/drain system: _____ feet

Slope of second liner/drain system: _____   percent
Distance from crest to drain in second liner/drain system: _____ feet

Slope of third liner/drain system: _____   percent
Distance from crest to drain in third liner/drain system: _____ feet

Slope of fourth liner/drain system: _____   percent
Distance from crest to drain in fourth liner/drain system: _____ feet

Initial quantity of snow or ice water on surface (not asked if
   program is to initialize the soil water): _____   inches

* If soil texture number is 19:   If soil texture number is 20:

If soil texture number is 19:		If soil texture number is 20:	
(a) wilting point _____	vol/vol	(a) wilting point _____	vol/vol
(b) field capacity _____	vol/vol	(b) field capacity _____	vol/vol
(c) porosity _____	vol/vol	(c) porosity _____	vol/vol
(d) saturated hydraulic conductivity _____	cm/sec	(d) saturated hydraulic conductivity _____	cm/sec

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**                                                                        **
**                                                                        **
**           HYDROLOGIC EVALUATION OF LANDFILL PERFORMANCE                **
**             HELP MODEL VERSION 3.04   (13 MARCH 1995)                  **
**                DEVELOPED BY ENVIRONMENTAL LABORATORY                    **
**                  USAE WATERWAYS EXPERIMENT STATION                     **
**           FOR USEPA RISK REDUCTION ENGINEERING LABORATORY              **
**                                                                        **
**                                                                        **
******************************************************************************
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PRECIPITATION DATA FILE:     C:\HELP3\FCLF1PRE.D4
TEMPERATURE DATA FILE:       C:\HELP3\FCLF1T.D7
SOLAR RADIATION DATA FILE:   C:\HELP3\FCLF1SR.D13
EVAPOTRANSPIRATION DATA:     C:\HELP3\FCLF1ET.D11
SOIL AND DESIGN DATA FILE:   C:\HELP3\FCLF1SD.D10
OUTPUT DATA FILE:            C:\HELP3\FCLF10.OUT
```

TIME: 14:23   DATE: 3/20/1995

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     TITLE:  UNO-VEN LANDFARM AREA 1: FINAL COVER SYSTEM DESIGN

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NOTE: INITIAL MOISTURE CONTENT OF THE LAYERS AND SNOW WATER WERE
        COMPUTED AS NEARLY STEADY-STATE VALUES BY THE PROGRAM.

                        LAYER 1

            TYPE 1 - VERTICAL PERCOLATION LAYER
                  MATERIAL TEXTURE NUMBER   9
        THICKNESS   =   30.00   INCHES
        POROSITY   =   0.5010 VOL/VOL
        FIELD CAPACITY   =   0.2840 VOL/VOL
        WILTING POINT   =   0.1350 VOL/VOL
        INITIAL SOIL WATER CONTENT =   0.3152 VOL/VOL
        EFFECTIVE SAT. HYD. COND. = 0.190000006000E-03 CM/SEC
      NOTE: SATURATED HYDRAULIC CONDUCTIVITY IS MULTIPLIED BY 3.00
             FOR ROOT CHANNELS IN TOP HALF OF EVAPORATIVE ZONE.

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LAYER 2
--------

TYPE 1 - VERTICAL PERCOLATION LAYER
MATERIAL TEXTURE NUMBER    5

| | | | |
|---|---|---|---|
| THICKNESS | = | 60.00 | INCHES |
| POROSITY | = | 0.4570 | VOL/VOL |
| FIELD CAPACITY | = | 0.1310 | VOL/VOL |
| WILTING POINT | = | 0.0580 | VOL/VOL |
| INITIAL SOIL WATER CONTENT | = | 0.1523 | VOL/VOL |
| EFFECTIVE SAT. HYD. COND. | = | 0.100000005000E-02 | CM/SEC |

GENERAL DESIGN AND EVAPORATIVE ZONE DATA
----------------------------------------

NOTE:  SCS RUNOFF CURVE NUMBER WAS COMPUTED FROM DEFAULT
       SOIL DATA BASE USING SOIL TEXTURE # 9 WITH A
       FAIR STAND OF GRASS, A SURFACE SLOPE OF  2.%
       AND A SLOPE LENGTH OF  650. FEET.

| | | | |
|---|---|---|---|
| SCS RUNOFF CURVE NUMBER | = | 80.90 | |
| FRACTION OF AREA ALLOWING RUNOFF | = | 100.0 | PERCENT |
| AREA PROJECTED ON HORIZONTAL PLANE | = | 5.500 | ACRES |
| EVAPORATIVE ZONE DEPTH | = | 20.0 | INCHES |
| INITIAL WATER IN EVAPORATIVE ZONE | = | 6.616 | INCHES |
| UPPER LIMIT OF EVAPORATIVE STORAGE | = | 10.020 | INCHES |
| LOWER LIMIT OF EVAPORATIVE STORAGE | = | 2.700 | INCHES |
| INITIAL SNOW WATER | = | 0.000 | INCHES |
| INITIAL WATER IN LAYER MATERIALS | = | 18.596 | INCHES |
| TOTAL INITIAL WATER | = | 18.596 | INCHES |
| TOTAL SUBSURFACE INFLOW | = | 0.00 | INCHES/YEAR |

EVAPOTRANSPIRATION AND WEATHER DATA
-----------------------------------

NOTE:  EVAPOTRANSPIRATION DATA WAS OBTAINED FROM
       CHICAGO              ILLINOIS

| | | | |
|---|---|---|---|
| STATION LATITUDE | = | 41.78 | DEGREES |
| MAXIMUM LEAF AREA INDEX | = | 2.00 | |
| START OF GROWING SEASON (JULIAN DATE) | = | 117 | |
| END OF GROWING SEASON (JULIAN DATE) | = | 290 | |
| EVAPORATIVE ZONE DEPTH | = | 20.0 | INCHES |
| AVERAGE ANNUAL WIND SPEED | = | 10.30 | MPH |
| AVERAGE 1ST QUARTER RELATIVE HUMIDITY | = | 71.00 | % |
| AVERAGE 2ND QUARTER RELATIVE HUMIDITY | = | 65.00 | % |
| AVERAGE 3RD QUARTER RELATIVE HUMIDITY | = | 70.00 | % |
| AVERAGE 4TH QUARTER RELATIVE HUMIDITY | = | 72.00 | % |

NOTE:  PRECIPITATION DATA WAS SYNTHETICALLY GENERATED USING

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              COEFFICIENTS FOR    CHICAGO          ILLINOIS

            NORMAL MEAN MONTHLY PRECIPITATION (INCHES)

 JAN/JUL      FEB/AUG      MAR/SEP      APR/OCT      MAY/NOV      JUN/DEC
 -------      -------      -------      -------      -------      -------
   1.60         1.31         2.59         3.66         3.15         4.08
   3.63         3.53         3.35         2.28         2.06         2.10



     NOTE:   TEMPERATURE DATA WAS SYNTHETICALLY GENERATED USING
             COEFFICIENTS FOR   CHICAGO          ILLINOIS

           NORMAL MEAN MONTHLY TEMPERATURE (DEGREES FAHRENHEIT)

 JAN/JUL      FEB/AUG      MAR/SEP      APR/OCT      MAY/NOV      JUN/DEC
 -------      -------      -------      -------      -------      -------
  21.40        26.00        36.00        48.80        59.10        68.60
  73.00        71.90        64.70        53.50        39.80        27.70



     NOTE:   SOLAR RADIATION DATA WAS SYNTHETICALLY GENERATED USING
             COEFFICIENTS FOR   CHICAGO          ILLINOIS
             AND STATION LATITUDE  =  41.78 DEGREES
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                   ANNUAL TOTALS FOR YEAR     1
-----------------------------------------------------------------------
                              INCHES       CU. FEET      PERCENT
                              --------     ----------    -------
PRECIPITATION                  30.45       607934.437    100.00

RUNOFF                          1.234       24641.164      4.05

EVAPOTRANSPIRATION             26.871      536473.000     88.25

PERC./LEAKAGE THROUGH LAYER 2   0.906344    18095.166      2.98

CHANGE IN WATER STORAGE         1.439       28724.783      4.72

SOIL WATER AT START OF YEAR    18.596      371269.656

SOIL WATER AT END OF YEAR      20.035      399994.437

SNOW WATER AT START OF YEAR     0.000           0.000      0.00

SNOW WATER AT END OF YEAR       0.000           0.000      0.00

  L WATER BUDGET BALANCE        0.0000          0.295      0.00
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                    ANNUAL TOTALS FOR YEAR     2
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                              INCHES        CU. FEET      PERCENT
                              --------      ----------    -------
PRECIPITATION                 35.90         716743.625    100.00

RUNOFF                        3.376       ·  67406.273      9.40

EVAPOTRANSPIRATION            25.120        501512.562     69.97

PERC./LEAKAGE THROUGH LAYER  2   6.542187    130614.758     18.22

CHANGE IN WATER STORAGE       0.861         17192.104      2.40

SOIL WATER AT START OF YEAR   20.035        399994.437

SOIL WATER AT END OF YEAR     17.987        359102.562

SNOW WATER AT START OF YEAR   0.000             0.000      0.00

SNOW WATER AT END OF YEAR     2.909         58083.973      8.10

ANNUAL WATER BUDGET BALANCE   0.0009           17.917      0.00

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                    ANNUAL TOTALS FOR YEAR     3
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                              INCHES        CU. FEET      PERCENT
                              --------      ----------    -------
PRECIPITATION                 44.40         886445.750    100.00

RUNOFF                        7.367         147082.094     16.59

EVAPOTRANSPIRATION            32.998        658803.312     74.32

PERC./LEAKAGE THROUGH LAYER  2   5.722653    114252.766     12.89

CHANGE IN WATER STORAGE       -1.760        -35143.176     -3.96

SOIL WATER AT START OF YEAR   17.987        359102.562

SOIL WATER AT END OF YEAR     18.881        376968.250

SNOW WATER AT START OF YEAR   2.909         58083.973      6.55

     WATER AT END OF YEAR     0.254          5075.119      0.57

ANNUAL WATER BUDGET BALANCE   0.0727         1450.704      0.16

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                ANNUAL TOTALS FOR YEAR    4
-----------------------------------------------------------------------
                                INCHES      CU. FEET    PERCENT
                                --------    ----------  -------
    PRECIPITATION               30.12       601345.812  100.00

    RUNOFF                       4.694       93711.437   15.58

    EVAPOTRANSPIRATION          26.203      523138.656   86.99

    PERC./LEAKAGE THROUGH LAYER  2   1.565103   31247.287    5.20

    CHANGE IN WATER STORAGE     -2.342      -46751.363   -7.77

    SOIL WATER AT START OF YEAR 18.881      376968.250

    SOIL WATER AT END OF YEAR   16.794      335292.000

    SNOW WATER AT START OF YEAR  0.254        5075.119    0.84

    SNOW WATER AT END OF YEAR    0.000           0.000    0.00

    ANNUAL WATER BUDGET BALANCE  0.0000         -0.198    0.00

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                ANNUAL TOTALS FOR YEAR    5
-----------------------------------------------------------------------
                                INCHES      CU. FEET    PERCENT
                                --------    ----------  -------
    PRECIPITATION               32.29       644669.875  100.00

    RUNOFF                       3.254       64958.199   10.08

    EVAPOTRANSPIRATION          26.416      527402.750   81.81

    PERC./LEAKAGE THROUGH LAYER  2   1.122165   22404.020    3.48

    CHANGE IN WATER STORAGE      1.497       29880.289    4.63

    SOIL WATER AT START OF YEAR 16.794      335292.000

    SOIL WATER AT END OF YEAR   18.291      365172.281

    WATER AT START OF YEAR       0.000           0.000    0.00

    SNOW WATER AT END OF YEAR    0.000           0.000    0.00

    ANNUAL WATER BUDGET BALANCE  0.0012         24.643    0.00
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ANNUAL TOTALS FOR YEAR   6

	INCHES	CU. FEET	PERCENT
PRECIPITATION	34.58	690389.875	100.00
RUNOFF	2.076	41437.781	6.00
EVAPOTRANSPIRATION	28.508	569162.375	82.44
PERC./LEAKAGE THROUGH LAYER 2	3.475655	69391.445	10.05
CHANGE IN WATER STORAGE	0.517	10328.771	1.50
SOIL WATER AT START OF YEAR	18.291	365172.281	
SOIL WATER AT END OF YEAR	18.775	374834.000	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.033	667.059	0.10
UAL WATER BUDGET BALANCE	0.0035	69.525	0.01

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ANNUAL TOTALS FOR YEAR   7

	INCHES	CU. FEET	PERCENT
PRECIPITATION	35.24	703566.625	100.00
RUNOFF	2.767	55244.355	7.85
EVAPOTRANSPIRATION	27.269	544419.187	77.38
PERC./LEAKAGE THROUGH LAYER 2	2.886456	57628.090	8.19
CHANGE IN WATER STORAGE	2.290	45719.898	6.50
SOIL WATER AT START OF YEAR	18.775	374834.000	
WATER AT END OF YEAR	21.098	421220.937	
SNOW WATER AT START OF YEAR	0.033	667.059	0.09
SNOW WATER AT END OF YEAR	0.000	0.000	0.00

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ANNUAL WATER BUDGET BALANCE   0.0278   555.086   0.08

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ANNUAL TOTALS FOR YEAR   8

	INCHES	CU. FEET	PERCENT
PRECIPITATION	35.13	701370.625	100.00
RUNOFF	4.407	87983.500	12.54
EVAPOTRANSPIRATION	25.832	515732.250	73.53
PERC./LEAKAGE THROUGH LAYER 2	4.073740	81332.227	11.60
CHANGE IN WATER STORAGE	0.818	16322.487	2.33
SOIL WATER AT START OF YEAR	21.098	421220.937	
SOIL WATER AT END OF YEAR	21.502	429291.781	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
⬤ WATER AT END OF YEAR	0.413	8251.652	1.18
ANNUAL WATER BUDGET BALANCE	0.0000	0.171	0.00

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ANNUAL TOTALS FOR YEAR   9

	INCHES	CU. FEET	PERCENT
PRECIPITATION	38.61	770848.687	100.00
RUNOFF	6.403	127828.828	16.58
EVAPOTRANSPIRATION	28.802	575023.125	74.60
PERC./LEAKAGE THROUGH LAYER 2	6.561858	131007.492	17.00
CHANGE IN WATER STORAGE	-3.156	-63010.887	-8.17
⬤ WATER AT START OF YEAR	21.502	429291.781	
SOIL WATER AT END OF YEAR	18.759	374532.562	
SNOW WATER AT START OF YEAR	0.413	8251.652	1.07

SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	0.095	0.00

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ANNUAL TOTALS FOR YEAR   10

	INCHES	CU. FEET	PERCENT
PRECIPITATION	30.75	613923.875	100.00
RUNOFF	2.598	51863.988	8.45
EVAPOTRANSPIRATION	24.386	486858.906	79.30
PERC./LEAKAGE THROUGH LAYER 2	3.349090	66864.586	10.89
CHANGE IN WATER STORAGE	0.418	8336.140	1.36
SOIL WATER AT START OF YEAR	18.759	374532.562	
SOIL WATER AT END OF YEAR	19.177	382868.687	
●W WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	0.248	0.00

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ANNUAL TOTALS FOR YEAR   11

	INCHES	CU. FEET	PERCENT
PRECIPITATION	25.85	516095.250	100.00
RUNOFF	2.832	56531.309	10.95
EVAPOTRANSPIRATION	22.029	439812.281	85.22
PERC./LEAKAGE THROUGH LAYER 2	1.897665	37886.871	7.34
●GE IN WATER STORAGE	-0.908	-18134.910	-3.51
SOIL WATER AT START OF YEAR	19.177	382868.687	
SOIL WATER AT END OF YEAR	17.847	356317.656	

	INCHES	CU. FEET	PERCENT
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.422	8416.140	1.63
ANNUAL WATER BUDGET BALANCE	0.0000	-0.298	0.00

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ANNUAL TOTALS FOR YEAR   12

	INCHES	CU. FEET	PERCENT
PRECIPITATION	28.81	575191.625	100.00
RUNOFF	1.726	34465.414	5.99
EVAPOTRANSPIRATION	23.175	462691.844	80.44
PERC./LEAKAGE THROUGH LAYER 2	1.467179	29292.223	5.09
CHANGE IN WATER STORAGE	2.441	48742.184	8.47
SOIL WATER AT START OF YEAR	17.847	356317.656	
WATER AT END OF YEAR	20.710	413475.969	
SNOW WATER AT START OF YEAR	0.422	8416.140	1.46
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	-0.014	0.00

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ANNUAL TOTALS FOR YEAR   13

	INCHES	CU. FEET	PERCENT
PRECIPITATION	31.56	630095.437	100.00
RUNOFF	3.221	64303.215	10.21
EVAPOTRANSPIRATION	24.719	493521.844	78.32
PERC./LEAKAGE THROUGH LAYER 2	3.571666	71308.320	11.32
CHANGE IN WATER STORAGE	0.041	822.533	0.13
SOIL WATER AT START OF YEAR	20.710	413475.969	

SOIL WATER AT END OF YEAR   20.751   414298.500

SNOW WATER AT START OF YEAR   0.000   0.000   0.00

SNOW WATER AT END OF YEAR   0.000   0.000   0.00

ANNUAL WATER BUDGET BALANCE   0.0070   139.564   0.02

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                    ANNUAL TOTALS FOR YEAR   14

                              INCHES   CU. FEET   PERCENT
                              --------   ----------   -------
PRECIPITATION   31.36   626102.625   100.00

RUNOFF   1.896   37853.910   6.05

EVAPOTRANSPIRATION   22.062   440469.687   70.35

PERC./LEAKAGE THROUGH LAYER 2 5.905656 117906.422   18.83

CHANGE IN WATER STORAGE   1.496   29872.350   4.77

SOIL WATER AT START OF YEAR   20.751   414298.500

SOIL WATER AT END OF YEAR   18.622   371779.062

SNOW WATER AT START OF YEAR   0.000   0.000   0.00

SNOW WATER AT END OF YEAR   3.626   72391.805   11.56

ANNUAL WATER BUDGET BALANCE   0.0000   0.228   0.00

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                    ANNUAL TOTALS FOR YEAR   15

                              INCHES   CU. FEET   PERCENT
                              --------   ----------   -------
PRECIPITATION   24.36   486347.562   100.00

RUNOFF   4.395   87746.930   18.04

EVAPOTRANSPIRATION   20.217   403627.812   82.99

PERC./LEAKAGE THROUGH LAYER 2 1.608255   32108.812   6.60

CHANGE IN WATER STORAGE   -1.920   -38328.250   -7.88

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	INCHES	CU. FEET	PERCENT
SOIL WATER AT START OF YEAR	18.622	371779.062	
SOIL WATER AT END OF YEAR	20.328	405842.594	
SNOW WATER AT START OF YEAR	3.626	72391.805	14.88
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0597	1192.261	0.25

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ANNUAL TOTALS FOR YEAR   16

	INCHES	CU. FEET	PERCENT
PRECIPITATION	30.70	612925.500	100.00
RUNOFF	1.585	31645.314	5.16
EVAPOTRANSPIRATION	26.480	528677.062	86.25
PERC./LEAKAGE THROUGH LAYER 2	2.500142	49915.336	8.14
CHANGE IN WATER STORAGE	0.135	2687.664	0.44
SOIL WATER AT START OF YEAR	20.328	405842.594	
SOIL WATER AT END OF YEAR	20.462	408530.250	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	0.086	0.00

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ANNUAL TOTALS FOR YEAR   17

	INCHES	CU. FEET	PERCENT
PRECIPITATION	38.44	767454.562	100.00
RUNOFF	3.699	73848.617	9.62
EVAPOTRANSPIRATION	32.693	652724.187	85.05
PERC./LEAKAGE THROUGH LAYER 2	2.524576	50403.152	6.57

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	INCHES	CU. FEET	PERCENT
CHANGE IN WATER STORAGE	-0.486	-9711.930	-1.27
SOIL WATER AT START OF YEAR	20.462	408530.250	
⬤L WATER AT END OF YEAR	19.925	397809.187	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.051	1009.137	0.13
ANNUAL WATER BUDGET BALANCE	0.0095	190.520	0.02

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                    ANNUAL TOTALS FOR YEAR   18

	INCHES	CU. FEET	PERCENT
PRECIPITATION	24.91	497328.312	100.00
RUNOFF	3.693	73728.508	14.82
EVAPOTRANSPIRATION	20.975	418763.094	84.20
⬤C./LEAKAGE THROUGH LAYER 2	2.194667	43816.527	8.81
CHANGE IN WATER STORAGE	-1.952	-38979.910	-7.84
SOIL WATER AT START OF YEAR	19.925	397809.187	
SOIL WATER AT END OF YEAR	18.023	359838.437	
SNOW WATER AT START OF YEAR	0.051	1009.137	0.20
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	0.071	0.00

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                    ANNUAL TOTALS FOR YEAR   19

	INCHES	CU. FEET	PERCENT
⬤IPITATION	39.41	786820.312	100.00
RUNOFF	6.221	124211.305	15.79
EVAPOTRANSPIRATION	23.846	476084.906	60.51

PERC./LEAKAGE THROUGH LAYER 2	5.005622	99937.250	12.70
CHANGE IN WATER STORAGE	4.331	86460.227	10.99
SOIL WATER AT START OF YEAR	18.023	359838.437	
SOIL WATER AT END OF YEAR	22.281	444847.531	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.073	1451.132	0.18
ANNUAL WATER BUDGET BALANCE	0.0063	126.655	0.02

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ANNUAL TOTALS FOR YEAR 20

	INCHES	CU. FEET	PERCENT
PRECIPITATION	34.99	698575.250	100.00
RUNOFF	5.233	104480.719	14.96
EVAPOTRANSPIRATION	24.832	495780.719	70.97
PERC./LEAKAGE THROUGH LAYER 2	4.567862	91197.367	13.05
CHANGE IN WATER STORAGE	0.354	7062.309	1.01
SOIL WATER AT START OF YEAR	22.281	444847.531	
SOIL WATER AT END OF YEAR	22.708	453360.969	
SNOW WATER AT START OF YEAR	0.073	1451.132	0.21
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0027	54.122	0.01

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AVERAGE MONTHLY VALUES IN INCHES FOR YEARS 1 THROUGH 20

	JAN/JUL	FEB/AUG	MAR/SEP	APR/OCT	MAY/NOV	JUN/DEC
PRECIPITATION						

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   ------------
    TOTALS           1.56     1.42     2.51     3.11     3.62     3.94
                     3.78     2.92     3.50     2.24     2.23     2.08

  STD. DEVIATIONS    0.64     0.65     1.40     1.67     1.86     2.09
                     1.75     1.72     1.68     1.27     1.02     1.00


  RUNOFF
  ------
    TOTALS           0.591    0.776    1.473    0.162    0.032    0.068
                     0.067    0.057    0.046    0.009    0.005    0.348

  STD. DEVIATIONS    0.705    0.614    1.158    0.390    0.106    0.227
                     0.170    0.114    0.104    0.031    0.019    0.459


  EVAPOTRANSPIRATION
  ------------------
    TOTALS           0.467    0.434    0.785    3.044    3.482    4.642
                     3.857    2.419    2.880    2.113    0.988    0.559

  STD. DEVIATIONS    0.100    0.068    0.472    0.525    1.065    1.070
                     1.719    1.482    0.987    0.620    0.199    0.141


  PERCOLATION/LEAKAGE THROUGH LAYER  2
  ------------------------------------
    TOTALS           0.2324   0.1729   0.1695   0.1272   0.4018   0.5526
                     0.4386   0.3670   0.2652   0.2110   0.2080   0.2263

  STD. DEVIATIONS    0.2259   0.1484   0.1215   0.0611   0.4439   0.5550
                     0.3506   0.2917   0.1305   0.0742   0.1500   0.2983
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      AVERAGE ANNUAL TOTALS & (STD. DEVIATIONS) FOR YEARS   1 THROUGH   20

                            INCHES   CU. FEET   PERCENT
                      --------------------   -------------   --------
  PRECIPITATION   32.89   (5.107)   656708.7   100.00

  RUNOFF   3.634 (1.7023)   72548.63   11.047

  EVAPOTRANSPIRATION   25.672 (3.3840)   512534.00   78.046

  PERCOLATION/LEAKAGE THROUGH   3.37243 (1.82428)   67330.508   10.25272
     LAYER 2

  CHANGE IN WATER STORAGE   0.206   (1.8462)   4104.57   0.625

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             PEAK DAILY VALUES FOR YEARS    1 THROUGH   20
         -----------------------------------------------------------------

                                            (INCHES)      (CU. FT.)
                                            ----------    --------------

         PRECIPITATION                      4.09          81656.852

         RUNOFF                             1.708         34097.8828

         PERCOLATION/LEAKAGE THROUGH LAYER  2   0.106136      2119.00269

         SNOW WATER                         4.36          87090.8984


         MAXIMUM VEG. SOIL WATER (VOL/VOL)          0.3994

         MINIMUM VEG. SOIL WATER (VOL/VOL)          0.1350

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         FINAL WATER STORAGE AT END OF YEAR   20
    ----------------------------------------------------------------
              LAYER        (INCHES)         (VOL/VOL)
              -----        --------         ---------
                1           9.6891           0.3230

                2          13.0187           0.2170

         SNOW WATER        0.000


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**                                                                  **
**                                                                  **
**          HYDROLOGIC EVALUATION OF LANDFILL PERFORMANCE           **
**          HELP MODEL VERSION 3.03  (31 DECEMBER 1994)             **
**          DEVELOPED BY ENVIRONMENTAL LABORATORY                   **
**              USAE WATERWAYS EXPERIMENT STATION                   **
**          FOR USEPA RISK REDUCTION ENGINEERING LABORATORY         **
**                                                                  **
**                                                                  **
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PRECIPITATION DATA FILE:       C:\HELP3\UNOPREC.D4
TEMPERATURE DATA FILE:         C:\HELP3\UNOTEMP.D7
SOLAR RADIATION DATA FILE:     C:\HELP3\UNOSOLR.D13
EVAPOTRANSPIRATION DATA:       C:\HELP3\UNOEVAP.D11
SOIL AND DESIGN DATA FILE:     C:\HELP3\UNOSOIL.D10
OUTPUT DATA FILE:              C:\HELP3\UNOOUT1.OUT


TIME:  17:46     DATE:   4/15/1996



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    TITLE:   UNO-VEN LANDFARM AREA 1: TREES PLANTED 3

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    NOTE:   INITIAL MOISTURE CONTENT OF THE LAYERS AND SNOW WATER
            WERE SPECIFIED BY THE USER.




                           LAYER   1
                           --------


              TYPE 1 - VERTICAL PERCOLATION LAYER
                   MATERIAL TEXTURE NUMBER    5
          THICKNESS                   =      30.00   INCHES
          POROSITY                    =      0.4570  VOL/VOL
          FIELD CAPACITY              =      0.1310  VOL/VOL
          WILTING POINT               =      0.0580  VOL/VOL
          INITIAL SOIL WATER CONTENT  =      0.1523  VOL/VOL
          EFFECTIVE SAT. HYD. COND.   = 0.100000005000E-02 CM/SEC
      NOTE:   SATURATED HYDRAULIC CONDUCTIVITY IS MULTIPLIED BY  4.20
              FOR ROOT CHANNELS IN TOP HALF OF EVAPORATIVE ZONE.
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                           LAYER  2
                           --------

                   TYPE 1 - VERTICAL PERCOLATION LAYER
                      MATERIAL TEXTURE NUMBER   5
        THICKNESS                      =     90.00   INCHES
        POROSITY                       =      0.4570 VOL/VOL
        FIELD CAPACITY                 =      0.1310 VOL/VOL
        WILTING POINT                  =      0.0580 VOL/VOL
        INITIAL SOIL WATER CONTENT     =      0.1523 VOL/VOL
        EFFECTIVE SAT. HYD. COND.      = 0.100000005000E-02 CM/SEC




             GENERAL DESIGN AND EVAPORATIVE ZONE DATA
             ----------------------------------------


      NOTE:   SCS RUNOFF CURVE NUMBER WAS COMPUTED FROM DEFAULT
              SOIL DATA BASE USING SOIL TEXTURE # 5 WITH AN
              EXCELLENT STAND OF GRASS, A SURFACE SLOPE OF  2.%
              AND A SLOPE LENGTH OF  650. FEET.

      SCS RUNOFF CURVE NUMBER              =     45.50
      FRACTION OF AREA ALLOWING RUNOFF     =    100.0      PERCENT
      AREA PROJECTED ON HORIZONTAL PLANE   =      5.500    ACRES
      EVAPORATIVE ZONE DEPTH               =     96.0      INCHES
      INITIAL WATER IN EVAPORATIVE ZONE    =     14.621    INCHES
      UPPER LIMIT OF EVAPORATIVE STORAGE   =     43.872    INCHES
      LOWER LIMIT OF EVAPORATIVE STORAGE   =      5.568    INCHES
      INITIAL SNOW WATER                   =      0.000    INCHES
      INITIAL WATER IN LAYER MATERIALS     =     18.276    INCHES
      TOTAL INITIAL WATER                  =     18.276    INCHES
      TOTAL SUBSURFACE INFLOW              =      0.00     INCHES/YEAR




                EVAPOTRANSPIRATION AND WEATHER DATA
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      NOTE:   EVAPOTRANSPIRATION DATA WAS OBTAINED FROM
                 CHICAGO                  ILLINOIS

          MAXIMUM LEAF AREA INDEX               =  3.00
          START OF GROWING SEASON (JULIAN DATE) =   117
          END OF GROWING SEASON (JULIAN DATE)   =   290
          AVERAGE ANNUAL WIND SPEED             = 10.30 MPH
          AVERAGE 1ST QUARTER RELATIVE HUMIDITY = 71.00 %
          AVERAGE 2ND QUARTER RELATIVE HUMIDITY = 65.00 %
          AVERAGE 3RD QUARTER RELATIVE HUMIDITY = 70.00 %
          AVERAGE 4TH QUARTER RELATIVE HUMIDITY = 72.00 %




      NOTE:   PRECIPITATION DATA WAS SYNTHETICALLY GENERATED USING
                 COEFFICIENTS FOR      CHICAGO              ILLINOIS
```

NORMAL MEAN MONTHLY PRECIPITATION (INCHES)

JAN/JUL	FEB/AUG	MAR/SEP	APR/OCT	MAY/NOV	JUN/DEC
1.60	1.31	2.59	3.66	3.15	4.08
3.63	3.53	3.35	2.28	2.06	2.10

NOTE: TEMPERATURE DATA WAS SYNTHETICALLY GENERATED USING
       COEFFICIENTS FOR   CHICAGO   ILLINOIS

NORMAL MEAN MONTHLY TEMPERATURE (DEGREES FAHRENHEIT)

JAN/JUL	FEB/AUG	MAR/SEP	APR/OCT	MAY/NOV	JUN/DEC
21.40	26.00	36.00	48.80	59.10	68.60
73.00	71.90	64.70	53.50	39.80	27.70

NOTE: SOLAR RADIATION DATA WAS SYNTHETICALLY GENERATED USING
       COEFFICIENTS FOR   CHICAGO   ILLINOIS

STATION LATITUDE = 41.78 DEGREES

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ANNUAL TOTALS FOR YEAR   1

	INCHES	CU. FEET	PERCENT
PRECIPITATION	30.45	607934.437	100.00
RUNOFF	0.247	4938.249	0.81
EVAPOTRANSPIRATION	30.264	604217.062	99.39
PERC./LEAKAGE THROUGH LAYER 2	0.343000	6847.991	1.13
CHANGE IN WATER STORAGE	-0.404	-8069.083	-1.33
SOIL WATER AT START OF YEAR	18.276	364879.750	
SOIL WATER AT END OF YEAR	17.872	356810.656	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	0.197	0.00

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                    ANNUAL TOTALS FOR YEAR      2
--------------------------------------------------------------------------------
                                       INCHES        CU. FEET      PERCENT
                                      --------      ----------     -------
 PRECIPITATION                         35.90        716743.625     100.00

 RUNOFF                                 1.222        24394.506       3.40

 EVAPOTRANSPIRATION                    32.054       639966.000      89.29

 PERC./LEAKAGE THROUGH LAYER   2        4.645391     92745.234      12.94

 CHANGE IN WATER STORAGE               -2.022       -40362.277      -5.63

 SOIL WATER AT START OF YEAR           17.872       356810.656

 SOIL WATER AT END OF YEAR             12.941       258364.422

 SNOW WATER AT START OF YEAR            0.000            0.000       0.00

 SNOW WATER AT END OF YEAR              2.909        58083.969       8.10

 ANNUAL WATER BUDGET BALANCE            0.0000           0.181       0.00

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                    ANNUAL TOTALS FOR YEAR      3
--------------------------------------------------------------------------------
                                       INCHES        CU. FEET      PERCENT
                                      --------      ----------     -------
 PRECIPITATION                         44.40        886445.750     100.00

 RUNOFF                                 2.173        43391.734       4.90

 EVAPOTRANSPIRATION                    34.180       682413.125      76.98

 PERC./LEAKAGE THROUGH LAYER   2        3.676013     73391.602       8.28

 CHANGE IN WATER STORAGE                4.370        87249.211       9.84

 SOIL WATER AT START OF YEAR           12.941       258364.422

 SOIL WATER AT END OF YEAR             19.966       398622.469

 SNOW WATER AT START OF YEAR            2.909        58083.973       6.55

 SNOW WATER AT END OF YEAR              0.254         5075.119       0.57

 ANNUAL WATER BUDGET BALANCE            0.0000           0.033       0.00

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                    ANNUAL TOTALS FOR YEAR      4
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                                    INCHES       CU. FEET      PERCENT
                                   --------     ----------     -------
PRECIPITATION                       30.12       601345.812     100.00

RUNOFF                               1.636       32666.117       5.43

EVAPOTRANSPIRATION                  31.934      637571.125     106.02

PERC./LEAKAGE THROUGH LAYER  2       4.562236    91085.047      15.15

CHANGE IN WATER STORAGE             -8.013     -159976.625     -26.60

SOIL WATER AT START OF YEAR         19.966      398622.469

SOIL WATER AT END OF YEAR           12.207      243720.969

SNOW WATER AT START OF YEAR          0.254        5075.119       0.84

SNOW WATER AT END OF YEAR            0.000           0.000       0.00

ANNUAL WATER BUDGET BALANCE          0.0000          0.162       0.00

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                    ANNUAL TOTALS FOR YEAR      5
----------------------------------------------------------------------
                                    INCHES       CU. FEET      PERCENT
                                   --------     ----------     -------
PRECIPITATION                       32.29       644669.875     100.00

RUNOFF                               1.191       23787.865       3.69

EVAPOTRANSPIRATION                  28.347      565957.375      87.79

PERC./LEAKAGE THROUGH LAYER  2       2.710140    54107.953       8.39

CHANGE IN WATER STORAGE              0.041         816.821       0.13

SOIL WATER AT START OF YEAR         12.207      243720.969

SOIL WATER AT END OF YEAR           12.248      244537.797

SNOW WATER AT START OF YEAR          0.000           0.000       0.00

SNOW WATER AT END OF YEAR            0.000           0.000       0.00

ANNUAL WATER BUDGET BALANCE          0.0000         -0.148       0.00

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              ANNUAL TOTALS FOR YEAR      6
------------------------------------------------------------------
                                  INCHES      CU. FEET    PERCENT
                                 --------    ----------   -------
PRECIPITATION                     34.58      690389.875   100.00

RUNOFF                            0.529       10559.822     1.53

EVAPOTRANSPIRATION               29.805      595047.250    86.19

PERC./LEAKAGE THROUGH LAYER  2    3.625921    72391.516    10.49

CHANGE IN WATER STORAGE           0.621       12391.139     1.79

SOIL WATER AT START OF YEAR      12.248      244537.797

SOIL WATER AT END OF YEAR        12.836      256261.875

SNOW WATER AT START OF YEAR       0.000           0.000     0.00

SNOW WATER AT END OF YEAR         0.033         667.059     0.10

ANNUAL WATER BUDGET BALANCE       0.0000          0.176     0.00

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              ANNUAL TOTALS FOR YEAR      7
------------------------------------------------------------------
                                  INCHES      CU. FEET    PERCENT
                                 --------    ----------   -------
PRECIPITATION                     35.24      703566.625   100.00

RUNOFF                            0.738       14731.040     2.09

EVAPOTRANSPIRATION               26.994      538944.062    76.60

PERC./LEAKAGE THROUGH LAYER  2    1.828627    36508.547     5.19

CHANGE IN WATER STORAGE           5.679      113382.922    16.12

SOIL WATER AT START OF YEAR      12.836      256261.875

SOIL WATER AT END OF YEAR        18.548      370311.844

SNOW WATER AT START OF YEAR       0.033         667.059     0.09

SNOW WATER AT END OF YEAR         0.000           0.000     0.00

ANNUAL WATER BUDGET BALANCE       0.0000          0.057     0.00
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                    ANNUAL TOTALS FOR YEAR   8

                                    INCHES   CU. FEET   PERCENT
                                   --------   ----------   -------
   PRECIPITATION   35.13   701370.625   100.00

   RUNOFF   1.328   26509.168   3.78

   EVAPOTRANSPIRATION   30.158   602102.687   85.85

   PERC./LEAKAGE THROUGH LAYER 2   4.829130   96413.586   13.75

   CHANGE IN WATER STORAGE   -1.185   -23655.266   -3.37

   SOIL WATER AT START OF YEAR   18.548   370311.844

   SOIL WATER AT END OF YEAR   16.950   338404.937

   SNOW WATER AT START OF YEAR   0.000   0.000   0.00

   SNOW WATER AT END OF YEAR   0.413   8251.651   1.18

   ANNUAL WATER BUDGET BALANCE   0.0000   0.438   0.00

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                    ANNUAL TOTALS FOR YEAR   9

                                    INCHES   CU. FEET   PERCENT
                                   --------   ----------   -------
   PRECIPITATION   38.61   770848.687   100.00

   RUNOFF   2.530   50501.945   6.55

   EVAPOTRANSPIRATION   31.299   624879.000   81.06

   PERC./LEAKAGE THROUGH LAYER 2   7.500980   149757.078   19.43

   CHANGE IN WATER STORAGE   -2.719   -54289.258   -7.04

   SOIL WATER AT START OF YEAR   16.950   338404.937

   SOIL WATER AT END OF YEAR   14.644   292367.312

   SNOW WATER AT START OF YEAR   0.413   8251.651   1.07

   SNOW WATER AT END OF YEAR   0.000   0.000   0.00

	INCHES	CU. FEET	PERCENT
ANNUAL WATER BUDGET BALANCE	0.0000	-0.067	0.00

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ANNUAL TOTALS FOR YEAR   10

	INCHES	CU. FEET	PERCENT
PRECIPITATION	30.75	613923.875	100.00
RUNOFF	0.345	6886.078	1.12
EVAPOTRANSPIRATION	25.694	512984.062	83.56
PERC./LEAKAGE THROUGH LAYER 2	4.179077	83435.273	13.59
CHANGE IN WATER STORAGE	0.532	10618.287	1.73
SOIL WATER AT START OF YEAR	14.644	292367.312	
SOIL WATER AT END OF YEAR	15.176	302985.625	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	0.162	0.00

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ANNUAL TOTALS FOR YEAR   11

	INCHES	CU. FEET	PERCENT
PRECIPITATION	25.85	516095.250	100.00
RUNOFF	0.886	17680.248	3.43
EVAPOTRANSPIRATION	24.865	496423.437	96.19
PERC./LEAKAGE THROUGH LAYER 2	2.597097	51851.039	10.05
CHANGE IN WATER STORAGE	-2.497	-49859.668	-9.66
SOIL WATER AT START OF YEAR	15.176	302985.625	
SOIL WATER AT END OF YEAR	12.257	244709.812	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00

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SNOW WATER AT END OF YEAR              0.422         8416.140       1.63

ANNUAL WATER BUDGET BALANCE            0.0000            0.200       0.00

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                    ANNUAL TOTALS FOR YEAR    12
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                               INCHES         CU. FEET       PERCENT
                               -------        ----------     -------
PRECIPITATION                   28.81       575191.625       100.00

RUNOFF                          0.526        10506.159         1.83

EVAPOTRANSPIRATION             24.529       489723.219        85.14

PERC./LEAKAGE THROUGH LAYER  2  1.475926     29466.861         5.12

CHANGE IN WATER STORAGE         2.279        45495.238         7.91

SOIL WATER AT START OF YEAR    12.257       244709.812

SOIL WATER AT END OF YEAR      14.957       298621.187

SNOW WATER AT START OF YEAR     0.422         8416.140         1.46

SNOW WATER AT END OF YEAR       0.000            0.000         0.00

ANNUAL WATER BUDGET BALANCE     0.0000           0.157         0.00

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                    ANNUAL TOTALS FOR YEAR    13
------------------------------------------------------------------------
                               INCHES         CU. FEET       PERCENT
                               -------        ----------     -------
PRECIPITATION                   31.56       630095.437       100.00

RUNOFF                          0.908        18134.826         2.88

EVAPOTRANSPIRATION             27.087       540787.375        85.83

PERC./LEAKAGE THROUGH LAYER  2  2.254217     45005.437         7.14

CHANGE IN WATER STORAGE         1.311        26167.602         4.15

SOIL WATER AT START OF YEAR    14.957       298621.187

SOIL WATER AT END OF YEAR      16.268       324788.781
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	INCHES	CU. FEET	PERCENT
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.030	598.950	0.10
ANNUAL WATER BUDGET BALANCE	0.0000	0.219	0.00

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ANNUAL TOTALS FOR YEAR   14

	INCHES	CU. FEET	PERCENT
PRECIPITATION	31.36	626102.625	100.00
RUNOFF	0.277	5536.277	0.88
EVAPOTRANSPIRATION	24.727	493683.406	78.85
PERC./LEAKAGE THROUGH LAYER 2	5.944512	118682.187	18.96
CHANGE IN WATER STORAGE	0.381	7601.739	1.21
SOIL WATER AT START OF YEAR	16.268	324788.781	
SOIL WATER AT END OF YEAR	13.053	260597.672	
SNOW WATER AT START OF YEAR	0.030	598.950	0.10
SNOW WATER AT END OF YEAR	3.626	72391.797	11.56
ANNUAL WATER BUDGET BALANCE	0.0300	598.983	0.10

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ANNUAL TOTALS FOR YEAR   15

	INCHES	CU. FEET	PERCENT
PRECIPITATION	24.36	486347.562	100.00
RUNOFF	1.709	34129.699	7.02
EVAPOTRANSPIRATION	22.778	454752.969	93.50
PERC./LEAKAGE THROUGH LAYER 2	1.829481	36525.594	7.51
CHANGE IN WATER STORAGE	-1.956	-39060.680	-8.03
SOIL WATER AT START OF YEAR	13.053	260597.672	

	INCHES	CU. FEET	PERCENT
SOIL WATER AT END OF YEAR	14.722	293928.781	
SNOW WATER AT START OF YEAR	3.626	72391.797	14.88
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	-0.029	0.00

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ANNUAL TOTALS FOR YEAR   16

	INCHES	CU. FEET	PERCENT
PRECIPITATION	30.70	612925.500	100.00
RUNOFF	0.137	2739.283	0.45
EVAPOTRANSPIRATION	27.977	558561.312	91.13
PERC./LEAKAGE THROUGH LAYER 2	2.438348	48681.613	7.94
CHANGE IN WATER STORAGE	0.147	2943.144	0.48
SOIL WATER AT START OF YEAR	14.722	293928.781	
SOIL WATER AT END OF YEAR	14.870	296871.937	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	0.152	0.00

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ANNUAL TOTALS FOR YEAR   17

	INCHES	CU. FEET	PERCENT
PRECIPITATION	38.44	767454.562	100.00
RUNOFF	1.212	24195.959	3.15
EVAPOTRANSPIRATION	31.797	634829.062	82.72
PERC./LEAKAGE THROUGH LAYER 2	2.605642	52021.633	6.78
CHANGE IN WATER STORAGE	2.825	56407.910	7.35

	INCHES	CU. FEET	PERCENT
SOIL WATER AT START OF YEAR	14.870	296871.937	
SOIL WATER AT END OF YEAR	17.644	352270.719	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.051	1009.137	0.13
ANNUAL WATER BUDGET BALANCE	0.0000	0.005	0.00

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ANNUAL TOTALS FOR YEAR   18

	INCHES	CU. FEET	PERCENT
PRECIPITATION	24.91	497328.312	100.00
RUNOFF	2.027	40475.207	8.14
EVAPOTRANSPIRATION	24.516	489471.062	98.42
PERC./LEAKAGE THROUGH LAYER 2	3.851598	76897.148	15.46
CHANGE IN WATER STORAGE	-5.485	-109515.414	-22.02
SOIL WATER AT START OF YEAR	17.644	352270.719	
SOIL WATER AT END OF YEAR	12.210	243764.422	
SNOW WATER AT START OF YEAR	0.051	1009.137	0.20
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	0.300	0.00

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ANNUAL TOTALS FOR YEAR   19

	INCHES	CU. FEET	PERCENT
PRECIPITATION	39.41	786820.312	100.00
RUNOFF	2.032	40561.816	5.16
EVAPOTRANSPIRATION	28.460	568200.250	72.21
PERC./LEAKAGE THROUGH LAYER 2	3.825245	76371.008	9.71

	INCHES	CU. FEET	PERCENT
CHANGE IN WATER STORAGE	5.093	101687.344	12.92
SOIL WATER AT START OF YEAR	12.210	243764.422	
SOIL WATER AT END OF YEAR	17.230	344000.625	
SNOW WATER AT START OF YEAR	0.000	0.000	0.00
SNOW WATER AT END OF YEAR	0.073	1451.132	0.18
ANNUAL WATER BUDGET BALANCE	0.0000	-0.090	0.00

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ANNUAL TOTALS FOR YEAR   20

	INCHES	CU. FEET	PERCENT
PRECIPITATION	34.99	698575.250	100.00
RUNOFF	1.771	35355.477	5.06
EVAPOTRANSPIRATION	28.438	567761.750	81.27
PERC./LEAKAGE THROUGH LAYER 2	3.998627	79832.586	11.43
CHANGE IN WATER STORAGE	0.783	15625.712	2.24
SOIL WATER AT START OF YEAR	17.230	344000.625	
SOIL WATER AT END OF YEAR	18.086	361077.469	
SNOW WATER AT START OF YEAR	0.073	1451.132	0.21
SNOW WATER AT END OF YEAR	0.000	0.000	0.00
ANNUAL WATER BUDGET BALANCE	0.0000	-0.271	0.00

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AVERAGE MONTHLY VALUES IN INCHES FOR YEARS   1 THROUGH   20

	JAN/JUL	FEB/AUG	MAR/SEP	APR/OCT	MAY/NOV	JUN/DEC
PRECIPITATION						

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   TOTALS                 1.56      1.42      2.51      3.11      3.62      3.94
                          3.78      2.92      3.50      2.24      2.23      2.08

   STD. DEVIATIONS        0.64      0.65      1.40      1.67      1.86      2.09
                          1.75      1.72      1.68      1.27      1.02      1.00

RUNOFF
------
   TOTALS                0.232     0.261     0.496     0.030     0.000     0.000
                         0.000     0.000     0.000     0.000     0.000     0.153

   STD. DEVIATIONS       0.364     0.286     0.560     0.110     0.000     0.000
                         0.000     0.000     0.000     0.000     0.000     0.245

EVAPOTRANSPIRATION
------------------
   TOTALS                0.563     0.704     1.611     2.340     3.105     6.119
                         5.575     2.666     2.626     1.773     0.700     0.512

   STD. DEVIATIONS       0.083     0.159     0.303     0.469     0.853     0.542
                         1.325     0.917     0.772     0.536     0.177     0.113

PERCOLATION/LEAKAGE THROUGH LAYER  2
------------------------------------
   TOTALS               0.1358    0.0962    0.0853    0.0599    0.1708    0.3598
                        0.8925    0.7149    0.3096    0.2654    0.1758    0.1701

   STD. DEVIATIONS      0.0642    0.0372    0.0276    0.0219    0.3527    0.5201
                        0.8442    0.6626    0.1871    0.1788    0.0875    0.0837
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      AVERAGE ANNUAL TOTALS & (STD. DEVIATIONS) FOR YEARS   1 THROUGH   20

	INCHES	CU. FEET	PERCENT
PRECIPITATION	32.89 (5.107)	656708.7	100.00
RUNOFF	1.171 (0.7178)	23384.07	3.561
EVAPOTRANSPIRATION	28.295 (3.1322)	564913.69	86.022
PERCOLATION/LEAKAGE THROUGH LAYER 2	3.43606 (1.64893)	68600.937	10.44617
CHANGE IN WATER STORAGE	-0.011 (3.3328)	-220.06	-0.034

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          PEAK DAILY VALUES FOR YEARS     1 THROUGH    20
      ------------------------------------------------------------------
                                          (INCHES)        (CU. FT.)
                                          ----------      -------------
          PRECIPITATION                     4.09           81656.852

          RUNOFF                            1.135          22670.0586

          PERCOLATION/LEAKAGE THROUGH LAYER  2    0.323709      6462.85498

          SNOW WATER                        4.36           87090.8984


          MAXIMUM VEG. SOIL WATER (VOL/VOL)             0.2064

          MINIMUM VEG. SOIL WATER (VOL/VOL)             0.0571

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                FINAL WATER STORAGE AT END OF YEAR    20
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                LAYER        (INCHES)        (VOL/VOL)
                -----        --------        ---------
                  1           6.1633          0.2054

                  2          11.9222          0.1325

        SNOW WATER           0.000

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